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THE CHEMICAL ACTION OF ULTRASONIC WAVES ON MACROMOLECULES

I. E. El'piner

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INTRODUCTION

The chemical action of ultrasonic waves on macromolecules has been studied by a number of workers. It is determined chiefly by processes of polymerisation or depolymerisation of these compounds, and the study of such processes has revealed a characteristic, strictly specific effect of ultrasonic vibrations on macromolecular structures (long-chain and branched). This in turn raises certain questions about the structure of solutions of macromolecules and the nature of their mechano-chemical reactions, which have been widely studied[1-5], and it also justifies an independent examination of the problems.

In view of our recently published article[6], it is unnecessary to give a detailed account of the general problems of the mechanism of the chemical action of ultrasonic waves, and we shall restrict ourselves to a short summary of the principal theories.

Most workers consider that the chemical action of ultrasonic waves results chiefly from cavitation phenomena produced in the liquid medium exposed to the waves[7-10]. Cavitation is greatly facilitated by the presence of gas-bubble nuclei in the liquid under study.

Cavitation phenomena in a liquid are associated with the production of mechanical forces which bring about rupture of the chemical bonds. There are indications that these forces are produced by the collapse (annihilation) of the cavitation bubbles which takes place in the compression phase along the propagation path of the ultrasonic wave[11,12] (mechanical cavitation theory).

According to other workers[13,14], the chemical processes may be brought about by mechanical forces which develop when the characteristic pulsation frequency of the gas bubbles in the liquid coincides with the ultrasonic frequency used (resonance cavitation theory). A similar suggestion is that the ultrasonic chemical processes are thermal in nature[15,16], in view of the possible development of large quantities of heat in the resonating gas bubbles.

Finally, the photoelectrochemical cavitation theory, based on the theoretical suggestions of Frenkel'[17], has gained wide acceptance. According to this theory, high electrical potential differences are set up in the cavity during the initial period of its development and lead to electronic breakdown of the cavity. The production of freely moving electrical charges in the cavity should result in the activation or ionisation of the molecules of gas or vapour present. There are grounds for considering that the initiation of chemical processes in ultrasonic fields is brought about chiefly by solvent molecules or gas atoms which have been activated or ionised in the cavity[18-21].

To some extent the photoelectrochemical cavitation theory has made it possible to clarify the nature of the primary products which bring about the various ultrasonic chemical reactions. This is particularly true of the analysis of such reactions in aqueous medium, which is almost the only medium in which observations have been made on oxidation and reduction reactions and the decomposition and synthesis of inorganic and organic substances[22-27]. The explanation

is that water is the most favourable medium for the production of electrical voltages in the cavitation bubbles formed by the action of ultrasonic waves. Furthermore, it is generally accepted that the initiation of chemical reactions in an aqueous medium irradiated by ultrasonic waves is brought about by the breakdown products of the water molecules – atomic hydrogen and free hydroxyl radicals. The breakdown of water molecules to form the extremely reactive, H· and OH· radicals takes place in the cavity as a result of the ionisation of the molecules by the moving charges.

In addition to water molecules, molecules of any gases present are also activated or ionised in the cavity under the action of the electrical charge, as indicated by the following facts. When distilled water saturated with hydrogen and nitrogen is exposed to ultrasonic waves, ammonia is produced[28]; when distilled water saturated with CO and H_2 is exposed, formaldehyde is formed, and in the presence of CO, H_2, and N_2, hydrocyanic acid is formed. The synthesis of an extremely complex substance with empirical formula $C_{10}H_7O_3Cl_2$ by the action of ultrasonic waves on water containing methylene chloride[29] apparently takes place by the same mechanism.

There are a number of other examples which indicate the important part played in the initiation of chemical reactions by molecules which, having entered the cavity in the gaseous state, are there activated or ionised[30].

The question of the possible appearance of electrical potential differences in cavities produced not in aqueous media but in organic solvents, particularly in non-polar solvents, is still unresolved. The problem arises since processes of polymerisation and depolymerisation of macromolecules under the action of ultrasonic waves take place not only in water but also in polar and non-polar organic liquids. In the theory of the action of ultrasonic waves on macromolecules, greatest attention has naturally been given to the part played in the depolymerising effect by the mechanical forces arising from the propagation of the acoustic energy in the liquid.

I. THE DEPOLYMERISING EFFECT OF ULTRASONIC WAVES AND CAVITATION PHENOMENA

The depolymerising action of ultrasonic waves on solutions of starch, gum arabic, and other macromolecular compounds was established by Szalay as early as 1933 [31]. The degradation of these compounds was accompanied by a decrease in the viscosity of the test solutions. In certain cases, however, this viscosity decrease was temporary and reversible; the viscosity of the solution returned to its original value on standing[32-35]. In other words, the action of the ultrasonic waves on the colloidal solutions led to the isothermal phenomenon known as thixotropy.

As a rule, the prolonged exposure of solutions of macromolecules to ultrasonic waves leads to a permanent, irreversible decrease in viscosity, indicating a breakdown in the molecular structure as a result of the rupture of valency bonds. The irreversible decrease in the viscosity of long-chain molecules was observed by Schmid and Rommel[36-39], who exposed dilute solutions of polyvinyl acetate, polyacrylic ester and nitrocellulose in organic solvents to the action of ultrasonic waves. The viscosity of the exposed solutions remained low even after the solvent had been carefully evaporated by heating and the residue redissolved.

These authors also noted similar phenomena under conditions which excluded oxidation processes and cavitation phenomena. They reported that degradation of long-chain molecules (nitrocellulose and polystyrene in toluene) was observed in a liquid exposed to ultrasonic waves, both in the absence of oxygen and under a constant external pressure of ~15 atm. It is known that the application of an external pressure of 4–5 atm to a liquid irradiated at the intensities used by the authors is sufficient to suppress cavitation.

In explaining the depolymerising effect of ultrasonic waves, Schmid considers two idealised cases: 1) the long-chain molecule is firmly fixed in the solution, and 2) the long-chain molecule may move freely in the solution. As an example, he analysed the behaviour of polystyrene in an ultrasonic field by representing the molecule as a long fibre, free from frictional forces, to which isolated spheres (benzene rings) with a radius of 3 Å are attached at equal distances from one another.

When the macromolecules are firmly fixed in the ultrasonic field, frictional forces should arise between the rapidly moving solvent molecules and these macromolecules. In this case the frictional forces may be calculated using Stokes' formula

$$f_0 = P_n 6\pi r \eta V_s, \qquad (1)$$

where η is the viscosity of the solvent, r the radius of the benzene ring, V_s the maximum rate at which the solvent molecules move as a result of the accelerations applied to them in the ultrasonic field, and P_n the number of links in the macromolecule.

Eqn. (1) may be written in the form

$$f_0 = \alpha P_n. \qquad (2)$$

Using the experimental data given by Jellinek and White[40]: $V_s = 50$ cm sec^{-1}, $r = 3$ Å, $\eta = 0.0062$ (in c.g.s. units), $P_n = 3000$, and hence $f_0 = 5.37 \times 10^{-4}$ dynes. According to de Boer's data[41], this value of f_0 is sufficient to break the C–C bond.

The forces acting on a macromolecule in an ultrasonic field will be smaller, by several orders of magnitude, if it is assumed that these molecules are free to move with the solvent molecules in the solution. These forces may be found from the formula

$$f_0 = P_n \frac{m}{N} \omega V_s, \qquad (3)$$

where m is the molecular weight of the monomer, N is Avogadro's number, $\omega = 2\pi/T$, and $T = 2.1 \times 10^{-6}$ sec (period of the ultrasonic wave). If the amplitude (A) of the acceleration in the vibrational motion is ωV_s, then the force acting on the macromolecule may be expressed by Eqn. (3).

Under the experimental conditions given above, $\frac{m}{N}\omega V_s$ will be equal to 2.77×10^{-14} dynes. In other words, in dilute solutions when there is no interaction between the dissolved molecules, the depolymerising effect should be zero, which is not in fact observed.

A slightly different treatment is given by Mark[42], from the following considerations. According to modern theory, long-chain molecules in dilute solution in suitable solvents are not extended to form straight chains, nor rolled up to form balls. The most probable configuration is a sinuous wavy structure. In solution, the separate links of the sinuous molecule undergo independent mechanical vibration and rotation at comparatively high rates (micro-Brownian intramolecular motion). The small links in the molecular

chain change position in a period of 10^{-3} sec. The chaotic movement of the molecules as a whole (macro-Brownian motion) is much slower. The average speed of the macromolecules amounts to 0.5–1.0 μ per second.

In an ultrasonic field, according to Mark, the movement of the whole macromolecule is much less than that of the solvent molecules, and according to his calculations, the frictional forces between the two greatly exceed the strengths of the chemical bonds C–C, C=C, and C=O. In accordance with spectroscopic data, these strengths are $4.5 \times \times 10^{-5}$ dynes, 5.77×10^{-5} dynes, and 9.77×10^{-5} dynes respectively. The frictional force between the macromolecules and solvent molecules (for speeds of the latter equal to 40 cm sec^{-1}) was estimated by Mark to be $2-3 \times 10^{-4}$ dynes per bond. This indicates that the application of ultrasonic waves to macromolecules containing the above groups should result in immediate breakdown to small molecules.

Schmid's experimental data show, however, that even on prolonged exposure to ultrasonic waves, only a very small fraction of the above-mentioned groups, when incorporated in a long-chain molecule, are in fact broken — approximately 5 per 1000. Mark therefore considers that most of the separate links of the macromolecule rotate freely around the line of the valency bond and follow the rapid vibrational movements of the solvent in the ultrasonic field, without offering any resistance to these movements. It is only rarely, in isolated places, that a considerable frictional force arises, capable of breaking the bond between the atoms.

It should be noted that the rotation of the separate links of high-polymer compounds is not free, but greatly restricted by interaction between the individual links of the molecule[43].

In addition, according to the theories of Kargin and Sogolova[44], Slonimskii et al.[45] (see also Kuz'minskii[46]), the stress produced in the micro-regions of the specimen (solid or liquid), at relatively small deformations, is not distributed uniformly and may be concentrated at isolated points, leading to the rupture of isolated covalent bonds in the macromolecule. This can apparently take place either in the compression or rarefaction regions along the propagation path of the ultrasonic wave, since the wave-length of the latter is much greater than the length of the macromolecule.

The views of Schmid and Mark have aroused considerable discussion, the only point not disputed being the equation put forward by Schmid to describe the kinetics of the breakdown of macromolecules in an ultrasonic field. This equation resulted from an analysis of the following experimental facts.

From a study of the influence of ultrasonic waves on solutions of separate fractions of polystyrene in toluene (molecular weight of 1st fraction 850 000, 2nd fraction 350 000, 3rd fraction 195 000), Schmid and Rommel established that during the first few minutes of the exposure the depolymerisation process is fairly rapid, after which the rate decreases and finally becomes zero as the molecular weight of the polymer approaches 30 000. The rate of depolymerisation is higher, the higher the original molecular weight, or, more precisely, the longer the initial length of the polymer studied. Analogous data have been obtained by Mostafa[47] (Fig. 1).

The same feature was observed by Schmid and Rommel in their investigation of the action of ultrasonic waves on dilute solutions of polyvinyl acetate, polymethyl-acrylate, nitrocellulose, and rubber.

The existence of a limiting degree of polymerisation was also established by Okuyama[48], and by Sato, Okuyama, and Chujo[49], who studied the action of ultrasonic waves on solutions of polyvinyl alcohol (initial molecular weight 77 000). The degree of polymerisation of the polymers studied, according to measurements of the diffusion and viscosity coefficients, reached limiting values after 90–120 minutes' exposure (frequency of vibrations 450 kc/s, intensity of ultrasonic waves 20 W/cm^2).

Schmid expressed this mathematically in the form

$$\frac{dx}{dt} = k(P_t - P_e) \qquad (4)$$

where x is the number of chemical bonds broken in unit volume for a given time of exposure, $\frac{dx}{dt}$ the rate of depolymerisation, P_t the degree of polymerisation of the long-chain molecule at time t, and P_e the limiting degree of polymerisation of the macromolecule when it undergoes no further depolymerisation under the influence of ultrasonic waves. This means that the rate of depolymerisation is independent of the chemical composition of the polymer; it depends on the difference between the initial and limiting degrees of polymerisation, and on the concentration of the irradiated polymer.

At very high degrees of polymerisation, Schmid observed a decrease in the rate of depolymerisation of the irradiated polymer. The decrease was particularly marked when the concentration of the macromolecules and the viscosity of the solution were high. In gels, the depolymerising effect was not observed at all.

Henglein[50] states that Schmid's equation is true for dilute solutions with concentrations up to 0.02 M, and that for higher concentrations the following equation is more satisfactory:

$$\frac{dx}{dt} = K \log \frac{P}{P_0}. \qquad (5)$$

Henglein suggests that ultrasonic depolymerisation may be brought about by the production of pulsating cavitation bubbles in the irradiated liquid. In the liquid close to these bubbles, velocity gradients may be produced resulting in the breakdown of the macromolecules. At high polymer concentrations, the oscillations of the bubbles are damped fairly rapidly, and Henglein suggests that this is associated with a decrease in the depolymerising effect of the ultrasonic waves under these conditions.

Weissler[51-53] claims that the depolymerisation of macromolecules is related to cavitation phenomena in the liquid. He observed the depolymerisation of polystyrene in toluene, and of hydroxyethylcellulose in water (frequency 175 kc/s) only when cavitation took place. According to his data, the molecular weight of the irradiated polymer decreased to one-tenth of its initial value.

In a degassed liquid, in which cavitation is difficult, Weissler observed no decrease in the molecular weight of the polymers (Fig. 2). His observations indicate that the depolymerisation of the macromolecules in the ultrasonic field is not related to the oxidation phenomena which take place in an aqueous medium exposed to ultrasonic waves (in the presence of oxygen). The depolymerisation of hydroxyethylcellulose in water was observed irrespective of

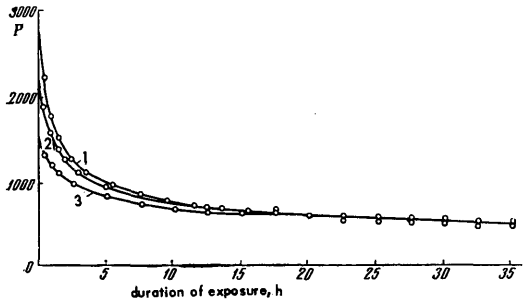


Fig. 1. Ultrasonic depolymerisation of polystyrene in benzene for different initial degrees of polymerisation P. 1) $P = 3260$; 2) $P = 2460$; 3) P 1505 (ultrasonic frequency 750 kc/s, intensity 12 W/cm^2)

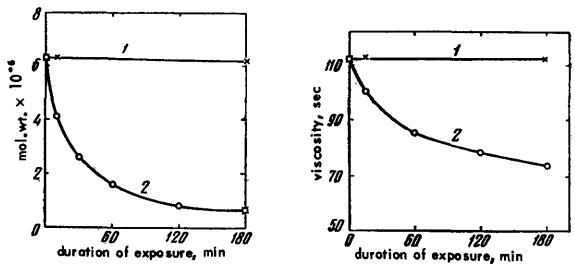


Fig. 2. a) Ultrasonic depolymerisation of polystyrene in toluene; b) ultrasonic depolymerisation of hydroxyethylcellulose in water. 1) Degassed solution; 2) in the presence of air.

whether the irradiated solution was saturated with air or helium.

Analogous conclusions were reached by Prudhomme and Grabar[54,55], who also studied the influence of ultrasonic waves on polystyrene in toluene and on carboxymethylcellulose in water (frequency 960 kc/s, intensity 6.8 W/cm^2). They observed the depolymerisation of the long-chain molecules when the irradiated liquid was saturated with gases that facilitate cavitation. In degassed liquid, or in liquid saturated with carbon dioxide, no depolymerisation took place.

More detailed studies on these lines were carried out by Brett and Jellinek[56]. According to their data, small cavitation bubbles and so-called cavitation noises are produced comparatively easily in irradiated benzene in the presence of nitrogen, hydrogen, argon, or methane, whereas cavitation is extremely slight in benzene saturated with ammonia or carbon dioxide, and is not observed at all in the presence of SO_2, even at ultrasonic intensities of 10 W/cm^2.

The above authors point out a definite correlation between the solubility of a gas in benzene and the intensity of the cavitation. The higher the solubility of the gas, the more readily it forms a molecularly dispersed solution, and the lower the tendency for the formation of bubble nuclei leading to cavitation.

Table 1 shows that various gases differ considerably in their solubility in benzene.

In this way the authors try to show that certain gases (N_2, H_2, O_2 and methane) intensify the ultrasonic depolymerisation of polystyrene in benzene, while NH_3, CO_2 or SO_2 inhibit this process. The same feature was observed by Gebert[57], who studied the action of ultrasonic waves on aqueous solutions of apple pectin in the presence of these gases.

The existence of a relationship between cavitation phenomena and the depolymerising action of ultrasonic waves was pointed out by Gaertner[58]. It is known that in the frequency range 400–1000 kc/s, the cavitation starts at comparatively low ultrasonic intensities (0.3–0.5 W/cm^2). At high frequencies (~ 2000 kc/s), more intense ultrasonic vibrations are required to produce cavitation. In accordance with this, Gaertner observed that on going to higher frequencies, the depolymerisation of long-chain molecules took place at intensities which always ensured cavitation. At a frequency of 2500 kc/s, the depolymerising effect (and also the cavitation) appeared only at very high intensities — 1.8 kW/cm^2.

TABLE 1. Solubility of various gases in benzene.

Gas	N_2	O_2	H_2	CO_2	NH_3	SO_2	CH_4	Air
Solubility of gas in ml/litre	0.10	0.219	0.07	2.40	9.95	8.8	0.54	0.140

There are reports, however, that cavitation only intensifies the degradation of macromolecules produced by mechano-hydrodynamic phenomena occurring in the liquid medium exposed to the ultrasonic waves. This possibility was admitted by Melville and Murray[59], who observed that the action of ultrasonic waves decreased the molecular weight of polystyrene in benzene from 700 000 to 260 000, with previous degassing of the solution. When the same solution was exposed to ultrasonic waves in the presence of air, the molecular weight of the polymer decreased to 47 000. According to the authors, the increase in the depolymerising effect in this case is due to the appearance of cavitation bubbles with resonance dimensions.

The intensifying action of cavitation on the rate of depolymerisation was later admitted by Schmid and coworkers[60]. However, they did not detect a relationship between the depolymerising effect and the frequency of the ultrasonic waves in the range 10–284 kc/s.

Schmid and Poppe[61] exclude the possibility that the breakdown of the polymer is due to resonance between the frequency of the molecular vibrations and the frequency of the ultrasonic waves being propagated in the liquid. The frequency of the ultrasonic vibrations (10^5–10^6) is usually smaller, by many orders of magnitude, than that of the molecular vibrations, estimated at 10^{14} c/s. The length of the ultrasonic waves in the liquid (1 mm to 1 cm) is many times greater than the length of the longest long-chain molecule, which is measured in microns.

Recently, attention has again been turned to the problem arising from the fact that the depolymerising action occurs under conditions excluding cavitation[47,62-63]. The authors of these papers excluded cavitation not only by removing the gases from the irradiated liquid, but also by using high frequencies.

According to Neppiras and Noltingk[64], there exists a limiting frequency (approximately 10 000 kc/s) above which no cavitation takes place. This limit depends on the initial dimensions of the bubbles in the liquid, on the amplitude of the ultrasonic wave pressure, and on the hydrostatic pressure in the liquid (see also other papers[65-67]). Gaertner states that there exist optimum frequencies at which cavitation is most intense, and that the cavitation is suppressed at frequencies exceeding 1000 or 2000 kc/s.

In agreement with this, Mostafa[63] found that the maximum degradation of polystyrene in benzene was observed at 1000 kc/s (intensity 12.5 W/cm²) (Fig.3). At higher frequencies, the rate of depolymerisation decreases considerably, but degradation of the macromolecules is still observed, even at frequencies of 2000 kc/s, at which, he believes, cavitation phenomena are absent. The same author also observed some degradation at these frequencies even in cases where the test solutions were degassed beforehand, which contradicts Weissler's findings[53]. In Mostafa's opinion, however, this discrepancy is due to the fact that Weissler observed the depolymerising effect at "medium" frequencies (400 kc/s) and comparatively low ultrasonic intensities (4 W/cm²). According to Mostafa, some degradation of macromolecules, albeit slight, still appears clearly at very high frequencies, i.e. in the absence of cavitation, probably as a result of resonance phenomena, and he believes that this is supported by the relationship which he has found between K in Eqn. (5) and the frequency of the ultrasonic waves.

From a practical point of view, the important feature is that cavitation phenomena are almost the only source of the mechanical forces which bring about the characteristic degradation of macromolecules when exposed to ultrasonic waves.

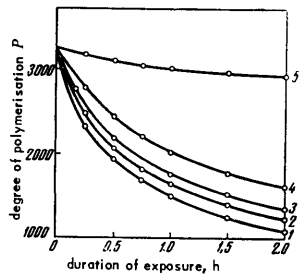


Fig. 3. Depolymerisation of 1% polystyrene in benzene under the action of ultrasonic waves of different frequency.
1) 1.0 Mc/s; 2) 1.25 Mc/s; 3) 0.75 Mc/s; 4) 1.25 Mc/s; 5) 2.0 Mc/s

II. THE HOMOGENISATION OF MACROMOLECULAR COMPOUNDS. THE FORMATION OF MACRORADICALS AND THEIR RECOMBINATION IN AN ULTRASONIC FIELD

One of the characteristic and remarkable phenomena produced by ultrasonic waves is a decrease in the polydispersity of the polymer under investigation. The homogenisation of a non-fractionated specimen of polymethyl-methacrylate under the influence of ultrasonic vibrations was first observed by Schmid, Paret, and Pfleiderer[60]. A specimen with uniform degree of polymerisation was obtained as the limiting degree of polymerisation P of the irradiated polymer was reached.

In a study of the influence of ultrasonic waves on aqueous solutions of polyvinyl alcohol, Sato, Okuyama, and Chujo[49] also discovered that the irradiated solutions become more uniform with respect to molecular weight. This phenomenon was not observed for depolymerisation brought about by heating or by oxidation with potassium permanganate. The authors suggest that in the last two cases, there is a high probability of rupture of the chemical bond at any part of the molecular chain, as a result of which the polymerisation products form a mixture of "fragments" of different molecular weight. In ultrasonic depolymerisation, however, the curve showing the molecular-weight distribution becomes narrower and sharper (Fig. 4) and the maximum is shifted to lower molecular weights.

The same authors believe that the action of ultrasonic waves leads to rupture of the molecule to form two equal parts, which in turn are broken into two equal parts, so that prolonged exposure leads to an almost uniformly dispersed polymer solution.

The question then arises of whether the ultrasonic depolymerisation is brought about by the rupture of weak bonds in the polymerised particles. In a study of this problem Melville and Murray[59] examined the rate of depolymerisation of polymethyl-methacrylate and two polymethyl--methacrylate–acrylonitrile copolymers differing in the molar ratios of methyl methacrylate and acrylonitrile (411 : 1 and 40 : 1). If it is considered that the bond rupture takes place at the points where the methyl methacrylate and acrylonitrile are joined, as has been shown for thermal depolymerisation[68], then these polymers should differ in the rate of depolymerisation under ultrasonic irradiation. Experiment showed, however, that there was no significant difference between the rates of breakdown of the irradiated copolymers (Table 2).

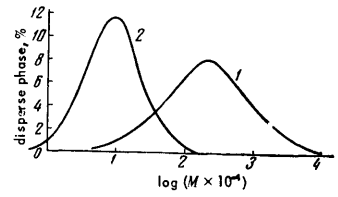


Fig. 4. Molecular-weight distribution curves. 1) Before irradiation; 2) after irradiation.

According to Schmid, Schneider, and Henglein[69], the predominant importance of mechanical forces in ultrasonic depolymerisation is indicated by the following effect. In the case of extremely long macromolecules, for which P is much greater than P_e, there is the possibility of rupture of bonds located at different points along the length of the molecular chain. As a result, the irradiated solution may contain molecular fragments of different length, which should lead to an increase in the polydispersity of the polymer at the beginning of the exposure period. In such cases, homogenisation of the solution takes place at a later stage of the exposure. This effect was detected experimentally[69]

TABLE 2. Molecular weight of polymers before and after ultrasonic irradiation (solvent—benzene, time of irradiation 350 min).

Polymer	Molecular weight of polymers	
	before irradiation	after irradiation
Methyl methacrylate	725 000	544 000±40 000
»	725 000	460 000±40 000
Methyl methacrylate—acrylonitrile	615 000	385 000±25 000
»	615 000	395 000±25 000

during the irradiation of fractionated polymethyl-methacrylate (mol. wt. 1.9×10^6). The authors calculated the molecular weight using Kuhn's equation, $Z_\eta = kM^a$. They also used the equation of Schulz and Blaschke[70], which makes it possible to determine the viscosity number directly from the measured specific viscosity:

$$Z_\eta = \frac{\eta_{sp}/c}{1 + k\eta_{sp}}.$$

The values of k and α for fractionated polymethacrylate were taken from the work of Schulz[71] and Meyerhoff and Schulz[72].

In the study of ultrasonic depolymerisation, the choice of values for the constants in the Staudinger and Kuhn equation becomes extremely difficult. The quantities α and k should remain constant for any degree of polymerisation of a given polymer, and for the calculation of these quantities it is necessary to determine the molecular weight by cryoscopic or ebullioscopic methods using the monomer or a low-molecular fraction of the polymer. According to many workers, however, the quantity k depends on the value of M.[62,73]

TABLE 3. Dependence of quantity of iodine consumed on the number of bonds broken in the irradiated polymer. (Polymer concentration 0.5 mole of monomer/litre; gas present argon).

Iodine concentration, 10^{-6} g-atoms × × litre^{-1}	Duration of exposure, min	Degree of polymerisation before irradiation, $P_0 \times 10^{-4}$	Degree of polymerisation after irradiation, $P_1 \times 10^{-3}$	Number of bonds broken, 10^{-6} moles/litre × litre^{-1} a	I_2 consumed 10^{-6} g-atoms × litre^{-1} b	b/a
41.1	25	1.90	2.40	1.82	4.00	2.20
21.4	25	1.90	2.30	1.91	4.32	2.25
10.8	15	1.90	2.75	1.55	3.02	1.95
5.0	8	1.90	4.60	0.83	1.75	2.11
1.8	5	1.90	7.50	0.40	0.91	2.27

The difficulties associated with the choice of k in calculating the degree of polymerisation of long-chain molecules explain the fact that P_e (and the number of bonds broken) for the same polymer is given different values by different authors[38,69,74-76].

More satisfactory data are apparently obtained by direct chemical determination of the number of molecular fragments formed as a result of rupture of the valency bonds. According to the theories developed by Kargin, Slonimskii, Sogolova, Baramboim, and others[1,2,77-81], extensive mechanical interaction not only causes the macromolecules to be displaced relative to one another, but also brings about mechanical rupture, accompanied by the appearance of free valencies at the ends of the broken polymeric chains. The rearrangement of polymer structure which develops under the influence of the high stresses is the essential feature of the process referred to by the authors as "chemical flow". The formation of macroradicals in this process brings about a number of chemical reactions such as mechano-chemical polymerisation, intensification of oxidation processes, ageing phenomena, etc.

It is useful to examine from this point of view the phenomena resulting from exposure to ultrasonic waves, since possible new methods controlling and directing these processes are then revealed.

Henglein[82] (see also Berlin[5]) considers that the rupture of a C–C bond in a long-chain molecule may give decomposition products in different physical states. In the so-called homolytic scission, two free radicals are formed:

$$P_{n+m} \rightarrow P_n^{\cdot} + P_m^{\cdot}.$$

In heterolytic scission, the products are ions of opposite charge:

$$P_{n+m} \rightarrow P_n^{+} + P_m^{-}.$$

Cases are also possible where the decomposition products become stable "fragments" of the broken macromolecule:

$$P_{n+m} \rightarrow P_n + P_m.$$

Experiment has shown that rupture of a C–C bond in an ultrasonic field results for the most part in the formation of long-chain radicals, which can be detected by their reaction with substances capable of indicating the presence of free radicals in solution.

When polyacrylic esters in benzene were exposed to ultrasonic waves in the presence of iodine, for example, the iodine reacted with the radicals formed. When the halogen was added after irradiation of the solution, no I_2 entered the long-chain molecule, indicating that the radical is short-lived[83].

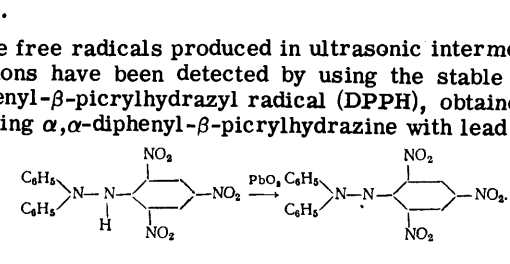
According to Henglein[83], the amount of I_2 reacting depends on the degree of polymerisation of the long-chain molecules exposed to the ultrasonic waves. The lower the degree of polymerisation, the lower the rate of depolymerisation under the ultrasonic irradiation, and the smaller the quantity of I_2 combining with the irradiated polymer. The author used the isotope I^{131}; if the reaction between I_2 and the irradiated polymer is

$$I_2 + P_{m+n} \rightarrow P_n^{\cdot} + P_m^{\cdot} + I_2 \rightarrow P_n I + P_m I,$$

then the number of I atoms which react should be double the number of bonds broken, as was in fact observed (Table 3).

When the polymer is exposed to ultrasonic waves in the presence of oxygen, only a very small fraction of the long-chain radicals formed combine with iodine, indicating that the C-radicals react more readily with oxygen than with iodine.

The free radicals produced in ultrasonic intermediate reactions have been detected by using the stable α,α-diphenyl-β-picrylhydrazyl radical (DPPH), obtained by oxidising α,α-diphenyl-β-picrylhydrazine with lead dioxide:

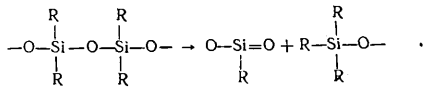


This compound (DPPH) is soluble in many organic solvents, and according to Bawn and Mellish[84], reacts readily with other free radicals. DPPH solutions have a violet colour and an intense absorption maximum at 520 mμ. This maximum decreases or disappears when the DPPH reacts with other free radicals in the solution.

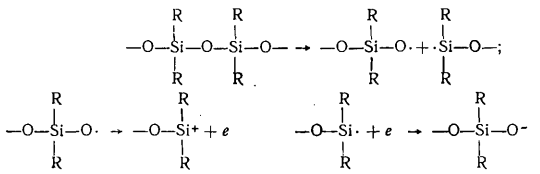
Henglein observed a decrease in the absorption maximum at 520 mμ when DPPH and the polymer under investigation were exposed simultaneously to ultrasonic waves, the decrease in the optical density of the DPPH solution being proportional to the number of broken C–C bonds in the macromolecule. On the basis of these studies, Henglein confirmed that the only macromolecules depolymerised under ultrasonic irradiation were those with degree of polymerisation above a definite value P_c. At P_c, no decrease in the quantity of DPPH was observed, i.e. the rate of depolymerisation at the limiting degree of polymerisation is zero. According to Henglein after the degree of polymerisation had reached 260, the exposure of polyacrylic esters to ultrasonic waves did not result in breakdown to form radicals capable of reacting with DPPH.

DPPH has also been used to detect the formation of long-chain free radicals when polystyrene and polyisobutylene in organic solvents are exposed to ultrasonic waves[86]. When a 3% solution of polyisobutylene in isooctane or benzene was exposed for 15 min, sufficient free radicals were produced to decolourise ~ 10 mg DPPH in 100 ml. The same authors also used DPPH to show that ultrasonic depolymerisation is apparently not always accompanied by the formation of long-chain free radicals. For example, no decrease in the quantity of DPPH was observed during the irradiation of 3% solutions of polydimethylsiloxane in benzene, *n*-heptane, or isooctane, although a considerable decrease in the viscosity of the solutions was brought about.

It may be suggested that under the influence of ultrasonic waves, polysiloxanes are split into compounds which, unlike long-chain radicals, do not react with DPPH. The authors believe that rupture of the Si–O bond may be accompanied by intramolecular disproportionation to produce two stable macromolecular fragments:



They also suggest that rupture of the Si–O bond leads to the formation of two radicals which can ionise:



The possibility of such processes was pointed out by Berlin[86], who believed that radical-ion formation may be observed where relatively unstable ionic bonds are present in the polymeric molecule,

$$\ldots\sim RCOOM\ldots\vdots\ldots OCOR_1\ldots\simeq\ldots\rightarrow\ldots\simeq\ldots RCOOM^+ + \sim R_1COO^-,$$

while long-chain radicals are formed for the most part when the polymeric chains contain covalent bonds only:

$$\ldots\sim R{-}CH_2\overset{\cdot}{\underset{\cdot}{\vdots}}CH_2{-}R_1\ldots\simeq\ldots\rightarrow\infty RCH_2^{\cdot} + {\cdot}CH_2R_1\ldots\simeq\ldots$$

Experimental proof of the possibility of heterolytic rupture of the Si–O bond is provided by the following observations made by the above mentioned authors. They exposed polysiloxane in benzene to the action of ultrasonic waves, in the presence of methanol labelled with C^{14}. Methanol reacts readily with $\geq C^+$ ions and probably also with $\geq Si^+$ ions, and this apparently explains the inclusion of the radioactive methanol in the fragments of the broken polymer. This inclusion is not prevented by the presence of DPPH in the irradiated solution. They state that labelled methanol does not react with the products of the ultrasonic rupture of polyisobutylene and polystyrene in organic solvents, which indicates that the C–C bond rupture in these compounds is homolytic. No methanol is taken up by these molecules, irrespective of whether or not DPPH is present in the solution.

On the assumption that one molecule of methanol is taken up for every bond broken in the polysiloxane, the authors calculated the number of bonds broken in the ultrasonic field, and obtained the value 19×10^{-7} moles of broken bonds per gram of polymer, which may prove sufficient to bring about extensive physicochemical changes in the system.

The authors obtained a similar low figure (8×10^{-7} per gram of substance) for the number of bonds broken in polyisobutylene exposed to ultrasonic waves, calculated from the quantity of DPPH disappearing, on the assumption that each broken bond uses up 2 molecules of DPPH.

If it is assumed that under the action of ultrasonic waves, the polysiloxane molecules split to form ions, then in organic solvents with low dielectric constants (particularly non-polar solvents), they should remain extremely close to one another. In the authors' opinion, this may (in the absence of methanol) facilitate the disproportionation and the production of stable long-chain fragments. This process apparently takes place rapidly, since the addition of the radioactive methanol immediately after ultrasonic irradiation is not accompanied by reaction with the breakdown products of the polysiloxane.

The formation of stable molecular "fragments" as a result of disproportionation can also take place when certain other polymers are exposed to ultrasonic waves, if substances capable of inactivating the long-chain radicals are not present in the solution. In the absence of such substances (I_2, O_2, DPPH, etc.), the long-chain radicals may also recombine. Studies on those lines have been carried out by Henglein[83,87], who determined the rate of scission of an irradiated polymer in the presence and in the absence of I_2. The difference in the values was used to estimate the number of radicals inactivated as a result of recombination and hence the probability of this process

$$w_k = \frac{\text{number of radicals inactivated by recombination}}{\text{number of radicals formed}}$$

If polymers in the presence of I_2 split from P_0 to P_1. and in the absence of I_2 from P_0 to P_1', then the corresponding number of broken bonds, in moles per litre, will be

$$x = c_\rho\left(\frac{1}{P_1}-\frac{1}{P_0}\right) \text{ and } x_1 = c_\rho\left(\frac{1}{P_1'}-\frac{1}{P_0}\right).$$

It may be assumed that the number of radicals inactivated by recombination amounts to $x-x_1=\Delta x$, and it can be shown that

$$\frac{\Delta x}{x} = \frac{\Delta P_1}{P_1'}\frac{P_0}{P_0-P_1}, \text{ where } \Delta P_1 = P_1'-P_1.$$

Assuming that P_0/P_0-P_1 is close to unity, Henglein obtained

$$\frac{\Delta x}{x} = \frac{\Delta P_1}{P_1'}.$$

From the Staudinger equation, he proposed the following formula:

$$\frac{\Delta P_1}{P_1'} = \frac{\Delta Z_{\eta_1}}{Z_{\eta_1}} \frac{1}{\alpha},$$

which is obtained by taking account of the fact that $Z_{\eta_1'} - Z_{\eta_1}$ is small compared to $Z_{\eta_1'}$.

The viscosity number Z_{η_1} was calculated according to Schulz and Blaschke, from the specific viscosity of the solution. The values of α for the polymethyl-methacrylate and polystyrene in benzene were taken from the literature [70,71].

Henglein worked with polymer solutions free from oxygen, which was displaced by argon. According to his data, the specific viscosity ($\eta_{1\,sp}$) of the polymethyl-methacrylate irradiated in the presence of I_2 differed from the value for the polymer exposed in the absence of I_2:

$$\eta_{1\,sp} = 0.837; \quad Z_{\eta_1} = 0.140;$$
$$\eta_{1\,sp}' = 0.922; \quad Z_{\eta_1'} = 0.152.$$

A greater difference was observed between the values of $\eta_{1\,sp}$ and $\eta_{1\,sp}'$ for irradiated solutions of polystyrene in benzene:

$$\eta_{1\,sp} = 0.927; \quad Z_{\eta_1} = 0.148;$$
$$\eta_{1\,sp}' = 1.167; \quad Z_{\eta_1'} = 0.177.$$

From this Henglein concluded that w_k is greater for polystyrene than for polymethyl-methacrylate.

III. THE FORMATION OF COPOLYMERS BY THE ACTION OF ULTRASONIC WAVES AND THE INFLUENCE OF THE LATTER ON THE RATE OF POLYMERISATION PROCESSES

The combination of macroradicals should be accompanied by copolymerisation processes when a mixture of polymers is exposed to ultrasonic waves. Thus Henglein showed that the value of w_k (the probability of radical combination) of an irradiated mixture of polystyrene and polymethyl-methacrylate dissolved in benzene is different from the value of w_k for the separate polymers in the same solution. Studies were made at identical concentrations (2.5 g per litre) of the polymers, which had almost identical degrees of polymerisation: P_0 for polystyrene = 1.0×10^4; P_0 for polymethyl-methacrylate = 1.3×10^4. The irradiated mixture of these polymers had $\eta_{1\,sp} = 0.916$ and $\eta_{1\,sp}' = 1.090$ ($Z_{\eta_1} = 0.160$, $Z_{\eta_1'} = 0.186$), which indicated that, under the influence of the ultrasonic waves, the polystyrene radicals recombine with polymethyl-methacrylate radicals to form block- or graft-copolymers:

$$R\text{----}R \rightarrow R_n^{\cdot} + R_m^{\cdot}; \quad Q\text{----}Q \rightarrow Q_n^{\cdot} + Q_m^{\cdot};$$
$$Q_n^{\cdot} + R_n^{\cdot} \rightarrow Q_n R_n, \text{ etc.}$$

Other experimental evidence for this process was obtained by the same author.

It is known that polymethyl-methacrylate is precipitated from a benzene solution containing polymethyl-methacrylate and polystyrene when carbon disulphide is added, and in this way it is possible to separate one polymer from the other. According to Henglein, however, no precipitate is obtained if the solution is first exposed to ultrasonic waves; the solution merely becomes turbid. In his opinion, this effect indicates a change in the structure of the polymers, namely the formation of graft-copolymers, which tend to form a colloidal solution in the presence of CS_2.

The tendency of graft-copolymers to form colloidal solutions in the presence of precipitants in which one of the components of the copolymer is soluble, is, according to Henglein, an exceptional phenomenon.

No graft-polymer formation takes place if the polymer mixture is exposed to the ultrasonic field in the presence of substances which inactivate the long-chain radicals — intermediate products of ultrasonic polymerisation (Table 4).

Table 4 shows that the combination of polymeric radicals of the same kind is influenced to a greater extent by DPPH and I_2 than by oxygen, which is inconsistent with the fact, established by the same author, that O_2 is a more powerful inactivator of long-chain radicals than DPPH or iodine.

According to Henglein, when a mixture of polymethyl-methacrylate and polystyrene is exposed to ultrasonic waves in the presence of O_2, the long-chain peroxy radicals formed,

$$P_n^{\cdot} + O_2 \rightarrow P_n\text{–O–O}^{\cdot} \text{ and } Q_n^{\cdot} + O_2 \rightarrow Q_n\text{–O–O}^{\cdot}$$

recombine as follows:

$$P_n\text{–O–O}^{\cdot} + Q_n^{\cdot} \rightarrow P_n\text{–O–O–}Q_n \text{ or}$$
$$P_n\text{–O–O}^{\cdot} + Q_n\text{–O–O}^{\cdot} \rightarrow P_n\text{–O–O–}Q_n + O_2.$$

The formation of graft-polymers is suppressed if, at identical concentration of the reacting components (polystyrene and polymethyl-methacrylate), one of these (polymethyl-methacrylate) has a comparatively low degree of polymerisation P (Table 5). This is explained as follows. The polystyrene, with large value of P, forms more long-chain radicals under the influence of ultrasonic waves than polymethyl-methacrylate. Under these conditions the long-chain radicals from the polystyrene will react with one another, and thus suppress the process of graft-copolymer formation.

Other investigators developed the idea that polymerisation processes in an ultrasonic field are brought about by the production of free radicals.

Thus the ultrasonic polymerisation of styrene in the presence of polystyrene, according to Berlin and El'tsefon [88], results from the fact that long-chain radicals — the products of scission of the polystyrene molecules — appear in the irradiated solution. According to these authors, the process is activated considerably when water is added to the

TABLE 4. Precipitation with CS_2 of polymethyl–methacrylate from an irradiated benzene solution of a mixture of polymethyl-methacrylate (1.5 g/litre, and polystyrene (1.5 g/litre). (P_0 of polystyrene = 1.0×10^4; P_0 of polymethyl–methacrylate = 1.3×10^4).

Duration of exposure, min	% of polymethyl–methacrylate precipitated in the presence of various substances capable of inactivating long-chain radicals			
	–*	I_2, 10^{-4} M	DPPH, 10^{-4} M	Air
5	0	93	—	60
10	0	98	90	60
60	0	97	—	80

* Solution saturated with argon.

TABLE 5. Precipitation with CS_2 of polymethylmethacrylate, with different degrees of polymerisation P, from benzene solutions of a mixture of polymethylmethacrylate (1.5 g/litre) and polystyrene (1.5 g/litre) (P for polystyrene = 1.0×10^4).

Degree of polymerisation of polymethylmethacrylate, P	Precipitate of polymethylmethacrylate formed during exposure for:	
	5 min	10 min
$1.3 \cdot 10^4$	0	0
$1.5 \cdot 10^3$	52	0
$4.3 \cdot 10^2$	80	35

irradiated reaction mixture. In this case the water molecules act as sources of free hydroxyl radicals, which, according to Berlin, accelerate the polymerisation of styrene.

Polymerisation reactions are shown by acrylonitrile in aqueous medium under the influence of ultrasonic waves [89]. The authors suggest that the polymerisation of the acrylonitrile takes place not only as a result of conversion of monomer to a radical form, but also as a result of a characteristic autocatalytic effect, by which the polyacrylonitrile molecules produced are depolymerised under the influence of the ultrasonic vibrations to form long-chain radicals which are able to increase their polymeric chain. Oxygen, which blocks the unsaturated end groups of the long-chain radical, is a fairly powerful inhibitor of the polymerisation of acrylonitrile.

TABLE 6. Dependence of the rate of polymerisation of acrylamide on the modulation frequency of the ultrasonic waves.

Modulation frequency, c/s	Duration of impulse, μ sec	Duration of exposure, min	Effective duration of exposure, min	Polymer formed, mg	η_{sp}/c (c = 1 g × × litre^{-1})	Rate of polymerisation, mole litre^{-1} × × min^{-1} × 10^{-4}
Unmodulated frequency	—	5	5	111	0.462	77
»	—	5	5	90	0.443	63
7	36.0	20	5	129	0.659	90
26	9.6	20	5	96	0.541	67
112	2.2	20	5	65	0.550	45
340	0.73	20	5	45	0.711	31
1200	0.21	40	10	10	—	3.5

The inhibiting action of oxygen may be intensified during ultrasonic depolymerisation in an aqueous medium as a result of its activation in the cavities.

The part played by cavitation in ultrasonic polymerisation is pointed out by Henglein [90]. According to his data, the rate of polymerisation of acrylamide in water saturated with argon depends on the duration of the ultrasonic impulse or on the modulation frequency of the ultrasonic vibrations (Table 6).

Table 6 shows that the rate of polymerisation decreases with decrease in the duration of the ultrasonic impulse, which also makes cavitation extremely difficult.

According to Henglein and Schulz [91], the rate and degree of polymerisation depend on the nature of the gas with which the solution is saturated. In the presence of nitrogen carefully purified from oxygen, the ultrasonic polymerisation of acrylamide starts with practically no induction period. The rate of polymerisation of acrylamide is also high when argon and nitrogen are present in the irradiated solution; the ultrasonic polymerisation is suppressed by oxygen and hydroquinone, which block the radicals produced.

Methacrylic acid is also polymerised in aqueous medium exposed to ultrasonic waves [92]. The data of these investigators show that the polymerisation effect is again dependent on the nature of the gas present in the water. Thus after 15 minutes' exposure in the presence of air, 1.8% of the methacrylic acid is polymerised, in the presence of nitrogen 12.7% is polymerised, and in the degassed solution the polymerisation process does not start at all.

Ultrasonic waves accelerate emulsion polymerisation. This has been observed in the preparation of copolymers of butadiene (CH_2=CH–CH=CH_2) and styrene (C_6H_5–CH=CH_2) [93] (see also Kudryavtsev [94]). 37.5 g of butadiene and 14.5 g of styrene in 90 ml of distilled water were irradiated, using soap as emulsifier and potassium persulphate as water—soluble initiator. The authors ascribe the increase in the rate of emulsion polymerisation and the decrease in the induction time of the reaction to the rapid removal of free oxygen from the mixture under the influence of the ultrasonic vibrations. In their view, the decrease in the induction period may be related to the activation of the polymerised styrene molecules by the ultrasonic waves, which should lead to an increase in the number of long-chain free radicals in the irradiated system. Finally, they suggest that any impurities acting as inhibitors of emulsion polymerisation may be oxidised in the ultrasonic field.

The acceleration of emulsion polymerisation in an ultrasonic field has been observed by other workers. For example, Sato and Harisaki [95] established that the action of ultrasonic vibrations increases the reaction yield in the emulsion polymerisation of vinyl acetate (CH_3COO–CH=CH_2). The initiator used was ammonium persulphate $(NH_4)_2S_2O_8$, and oleates were used as emulsifiers.

These examples indicate that water is a very favourable medium for the acceleration and possibly also the initiation of ultrasonic polymerisation of synthetic polymers. The medium is favourable not only for occurrence of cavitation phenomena and the related mechanical forces, but also for the electrochemical processes which take place in the cavities and result in the production of activated and ionised molecules of the solvent (water) and any gases present. These processes have to be taken into account, particularly in analysis of the depolymerising and polymerising action of ultrasonic vibrations on aqueous solutions of highly polymerised materials extracted from plant and animal cells, such as polysaccharides, nucleic acids, nucleoproteins, hyaluronic acids, etc. [96-102]

These macromolecules may be depolymerised under the influence of ultrasonic waves, and, under certain conditions, the opposite effect of increase in the molecular weight may be observed, apparently accompanied by an increase in the degree of branching. Such studies are of interest in examining the relationship between the biological function and structure of bio-polymers, and require a separate discussion.

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There is now sufficient information to indicate that modern mechano-chemistry has available a new form of energy — — ultrasonic energy — which is capable of bringing about almost all the reactions known in this field.

A clear picture has been obtained of the part played by a number of factors, such as the nature of the solvent and any

gases present, the physical parameters of the polymeric molecules, their concentration, etc., in bringing about the process known in mechano-chemistry as "destruction–combination" under the influence of ultrasonic waves.

Further study of ultrasonic macromolecular reactions promises the discovery of new principles in macromolecular chemistry and the extension of its practical applications.

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DEVELOPMENTS IN THE CHLORINATION OF SATURATED HYDROCARBONS

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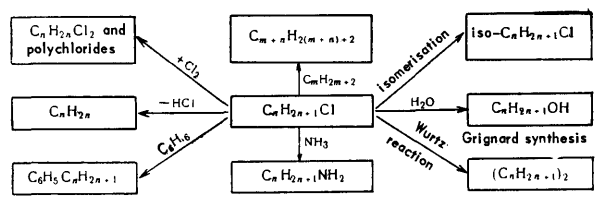
INTRODUCTION

The present article is a review of work published on the chlorination of saturated hydrocarbons in the USSR and abroad from 1947 to 1958.

Ellis[1] has reviewed the literature in this field up to 1934, and Hass and McBee[2] and Nelles[3] have also considered certain aspects of the chlorination of saturated hydrocarbons in their reviews. The literature from 1937 to 1947 has been reviewed by Solodar' and Markin[4].

A considerable expansion of the chemical industry in the USSR is planned for the period 1958–1965, particular attention being directed towards the necessity of utilising natural and industrial petroleum gases as raw material for the chemical industry. The saturated hydrocarbons in natural and industrial gases can be converted into useful products by various methods, chiefly by chlorination.

Diagram of possible conversions of alkyl halides



Chlorinated hydrocarbons find very wide application in industry and agriculture as solvents, refrigerants, synthetic intermediates, insecticides, herbicides, etc. At the present time the production of chlorinated hydrocarbons is growing continuously; thus in the USA the production of chlorine, hydrogen chloride, and chlorine-containing chemicals increased considerably in 1955 by comparison with 1954 [5] (Table 1).

TABLE 1. Production of chlorinated hydrocarbons in the USA (tons).

Product	1953	1954	1955	1956
Cl_2	—	2 622 298	3 091 628	—
HCl	—	672 889	764 419	—
CH_3Cl	18 300	—	16 500	—
CH_2Cl_2	28 000	—	31 000	—
$CHCl_3$	11 500	—	18 300	—
CCl_4	117 000	—	130 500	136 200
$C_2H_4Cl_2$	—	—	213 600	249 700
C_2H_3Cl	234 000	—	245 900	28 600

Chlorinated hydrocarbons may be obtained by various methods, the chief being:

1. Hydrochlorination and chlorination of unsaturated hydrocarbons:

$$C_nH_{2n} + HCl \rightarrow C_nH_{2n+1}Cl.$$

2. Chlorination of saturated hydrocarbons:

$$C_nH_{2n+2} + Cl_2 \rightarrow C_nH_{2n+1}Cl + HCl.$$

Both methods have considerable theoretical and practical interest.

The classic work of Butlerov and Markovnikov[6] on the mutual influence of atoms in organic molecules and the formulation of rules for the chlorination of alkanes has made a large contribution to the theoretical basis of the hydrochlorination of unsaturated hydrocarbons and the chlorination of saturated hydrocarbons. The ten general rules for the chlorination of saturated paraffinic hydrocarbons formulated by Hass et al.[7] represent a further development of Markovnikov's rules for the replacement of hydrogen atoms in hydrocarbons of the methane series.

Tishchenko's experimental data[8] confirm Markovnikov's theoretical propositions; in the chlorination of a saturated hydrocarbon the chlorine atom is more easily attached to a carbon atom already substituted by chlorine. By analysing published data[10-13], Ewell[9] has established a connection between the rate of replacement of hydrogen in the chlorination of saturated and unsaturated hydrocarbons, and the molecular structure of the hydrocarbon.

Later work by Soviet chemists on the chlorination of saturated hydrocarbons[14-29] shows that this field of chemistry is of great significance both for the further development of the Butlerov theory of the structure of organic compounds, and in practical application in Soviet industry.

I. THE CHAIN MECHANISM FOR THE CHLORINATION OF SATURATED HYDROCARBONS

In the theoretical and experimental study of the chain mechanism, much credit is due to Semenov and his school[14,15,16,29], who proved the chain mechanism for the chlorination of saturated hydrocarbons and explained the mechanism in the light of modern theory. The chain mechanism for the photochlorination reaction must be considered as firmly established, in agreement with Hass[30], who connects the initial formation of chain centres with the photochemical decomposition of chlorine:

$$Cl_2 + h\nu \rightarrow Cl\cdot + Cl\cdot .$$

The photochemical reaction between hydrogen and chlorine, which proceeds at room temperature, has been the most studied. Comparison of the number of light quanta absorbed with the number of molecules reacted shows that each molecule activated by light produces up to 10^5 molecules of hydrogen chloride. The reaction chains commence with chlorine atoms:

$$\left.\begin{array}{ll} 1) & Cl_2 + h\nu \rightarrow Cl\cdot + Cl\cdot , \\ 2) & Cl\cdot + H_2 \rightarrow HCl + H\cdot , \\ 3) & H\cdot + Cl_2 \rightarrow HCl + Cl\cdot , \end{array}\right\} \text{repeated.}$$

The photochemical chlorination of hydrocarbons is completely analogous to the reaction between hydrogen and chlorine. This has been confirmed experimentally by Jones and Bates[31] and Stewart and Weidenbaum[32], who studied the photochlorination of pentane in the liquid phase; they give the reaction mechanism as follows:

$$\left.\begin{array}{ll} 1) & Cl_2 + h\nu \rightarrow Cl\cdot + Cl\cdot , \\ 2) & Cl\cdot + C_5H_{12} \rightarrow C_5H_{11}\cdot + HCl, \\ 3) & C_5H_{11}\cdot + Cl_2 \rightarrow C_5H_{11}Cl + Cl\cdot , \end{array}\right\} \text{repeated.}$$

Numerous Soviet and foreign investigators have studied the mechanism of the chlorination of alkanes[10,29-35].

From experimental data, Pease and Walz[33] and others consider the chlorination of saturated hydrocarbons to be a chain reaction:

$$\left.\begin{array}{ll} 1) & Cl_2 \rightarrow Cl\cdot + Cl\cdot , \\ 2) & Cl\cdot + RH \rightarrow R\cdot + HCl, \\ 3) & R\cdot + Cl_2 \rightarrow RCl + Cl\cdot , \end{array}\right\} \text{chain.} \qquad (I)$$

However, thermal chlorination could proceed by a different mechanism:

$$\left.\begin{array}{ll} 1) & Cl_2 \rightarrow Cl\cdot + Cl\cdot , \\ 2) & RH + Cl\cdot \rightarrow RCl + H\cdot , \\ 3) & H\cdot + Cl_2 \rightarrow HCl + Cl\cdot , \end{array}\right\} \text{chain.} \qquad (II)^{36}$$

The fact that hydrogen has not been detected in the reaction products throws grave doubts on mechanism (II). The type (I) mechanism is supported by Vaughan and Rust[10], who showed that the chlorination of, for instance, propane is greatly accelerated in the presence of compounds which can furnish free radicals under the experimental conditions. The authors of the present review consider that the following may be adduced as proof of mechanism (I): reaction (2) of mechanism (I) is exothermic, while reaction (2) of mechanism (II) is endothermic, so that mechanism (I) is thermodynamically more probable.

Experimental data[10,29,31-35,37-42] indicate that the chlorination of methane may be represented as follows:

$$Cl_2 + h\nu \rightarrow Cl\cdot + Cl\cdot \quad -57.8 \text{ kcal},$$

1) $Cl\cdot + CH_4 \rightarrow HCl + CH_3\cdot$ (-101 + 102) + 1.0 kcal,

2) $CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$ (-57.8 + 83.5) + 25.7 kcal,

3) $CH_3Cl + Cl\cdot \rightarrow HCl + CH_2Cl\cdot$ (-97.4 + 102) + 4.6 kcal,

4) $CH_2Cl\cdot + Cl_2 \rightarrow CH_2Cl_2 + Cl\cdot$ (-57.8 + 78.5) + 20.7 kcal,

5) $CH_2Cl_2 + Cl\cdot \rightarrow HCl + CHCl_2\cdot$ (-93.2 + 102) + 8.8 kcal,

6) $CHCl_2\cdot + Cl_2 \rightarrow CHCl_3 + Cl\cdot$ (-57.8 + 73.5) + 15.7 kcal,

7) $CHCl_3 + Cl\cdot \rightarrow HCl + CCl_3\cdot$ (-89 + 102) + 13.0 kcal,

8) $CCl_3\cdot + Cl_2 \rightarrow CCl_4 + Cl\cdot$ (-57.8 + 68.4) + 10.6 kcal.

If the reaction is exothermic, according to the Polanyi–Evans rule[43]

$$E = 11.5 - 0.25\,g,$$

where E is the energy of activation and g the heat of reaction. Calculating the energy of activation for each stage of the reaction, we obtain

$$E_1 = 11.5 - 0.25 \times 1 = 11.25 \text{ kcal},$$
$$E_3 = 11.5 - 0.25 \times 4.6 = 10.35 \text{ kcal},$$
$$E_5 = 11.5 - 0.25 \times 8.8 = 9.3 \text{ kcal},$$
$$E_7 = 11.5 - 0.25 \times 13.0 = 8.25 \text{ kcal}.$$

The rates of reaction are for example:

$$v_1 = k_1 P_{CH_4} P_{Cl}$$
$$v_3 = k_3 P_{CH_3Cl} P_{Cl}$$
$$k_1 = f_1 z_1 e^{-\frac{E_1}{RT}}$$
$$k_3 = f_3 z_3 e^{-\frac{E_3}{RT}},$$

where k_1 and k_3 are the velocity constants of the corresponding reactions, f_1 and f_3 are the steric factors, and z_1 and z_3 are the collision numbers.

Therefore $\frac{v_1}{v_3} = \frac{k_1 P_{CH_4}}{k_3 P_{CH_3Cl}}$; and, when $\frac{P_{CH_4}}{P_{CH_3Cl}} = 1$ and with $f_1 = f_3$ and $z_1 = z_3$,

$$\frac{v_1}{v_3} = e^{\frac{E_3 - E_1}{RT}}$$

It follows from these calculations that the rates of chlorination of methane and its chlorinated derivatives are in the order

$$CHCl_3 > CH_2Cl_2 > CH_3Cl > CH_4.$$

The catalytic chlorination takes place by the general cationic substitution mechanism, i.e. the chlorine anion combines with the proton, and the chlorine cation with the hydrocarbon anion[44]:

$$\geq C - H \rightarrow \geq \overline{C} + H^+ \rightarrow \xrightarrow{CH + Cl^-} \geq C - Cl + HCl.$$

In initiated chlorination, the chlorine molecules are split into atoms by introducing into the reaction zone substances capable of forming free radicals, which then initiate the chain:

$$R - R \rightarrow 2R\cdot,$$

$$R\cdot + Cl_2 \rightarrow Cl\cdot + RCl,$$

$$Cl\cdot + C_nH_{2n+2} \rightarrow C_nH_{2n+1}\cdot + HCl,$$

$$C_nH_{2n+1}\cdot + Cl_2 \rightarrow C_nH_{2n+1}Cl + Cl\cdot, \text{ etc.}$$

Surfaces have a great influence on gas-phase chain reactions. The breaking of the chains on the wall of the reaction vessel, discovered by Semenov and his coworkers early in the development of the theory of chain reactions, must apparently be considered as the capture of a radical by the solid surface, forming a chemical compound (perhaps unstable) with it[45]. The wall may have a retarding influence on the chain reaction. The formation of a bond between the radical and the solid surface requires a certain energy of activation, which depends on the radical and the nature of the surface and sometimes reaches comparatively high values of the order of 9–10 kcal. The ability of various surfaces to combine with the active centres causes large changes in the general kinetics of the process.

The heterogeneous retardation of a homogeneous reaction was first studied experimentally by Trifonov[46], who established that in the photochemical reaction of hydrogen with chlorine, chlorine atoms are captured by the wall.

In addition to the breaking of chains, the solid surface has a large influence on the initiation of chains. Changes occurring in the reaction surface suggest a two-fold influence of the surface on the rate of chlorination. After the surface becomes covered with alkyl groups, the rate of reaction increases; the surface film may be more effective than clean Pyrex in initiating chains in thermal chlorination.

The accelerating effect of glass walls on the chlorination of ethane, studied by Vaughan and Rust[10], shows that chains are initiated on the surface in thermal chlorination.

Chambers and Ubbelohde[47] have observed that a film which does not contain chlorine compounds is formed on the wall of the reaction vessel in the chlorination of hydrocarbons. Since the film is removed by oxidation, it must be formed by the attack of the glass surface by alkyl radicals, with the formation of Si–O–R groups. These workers also showed that the rate of reaction of chlorine atoms with paraffinic hydrocarbons increases as the chain length of the hydrocarbon increases.

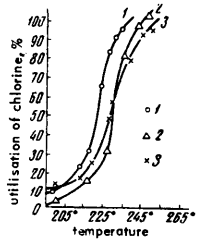


Fig. 1. Influence of the degree of branching of hydrocarbons on the relative rates of their thermal chlorination.
1) n-hexane; 2) 2, 3-dimethylbutane; 3) 2, 2, 4-trimethylpentane.

Fig. 1 shows that the rate of chlorination decreases with increased branching of the hydrocarbon chain.

II. THERMAL CHLORINATION OF SATURATED HYDROCARBONS

The thermal chlorination of paraffinic hydrocarbons is carried out industrially at 400°–600°, a temperature range which ensures a fairly fast reaction, usually under conditions of complete utilisation of the chlorine, thus avoiding the need to purify the reaction products from free chlorine. It appears that homogeneous bimolecular reactions also occur, in addition to chain reactions[10].

It is known that pyrolysis of the starting materials and the chlorination products takes place to a greater or lesser extent during the thermal chlorination of saturated hydrocarbons at sufficiently high temperatures; some isomerisation of the intermediate products also occurs. Polychlorides may therefore be produced not only by further chlorination of the monochloride, but also by chlorination of the products of pyrolysis and isomerisation.

1) Thermal Chlorination of Methane

In the chlorination of saturated hydrocarbons, that of methane has been most studied, because methane is abundant and because all its chloro-derivatives are economically important.

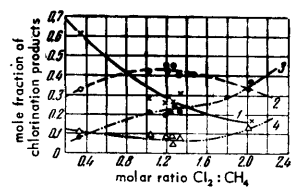


Fig. 2. Composition of the chlorination products of methane.
1) CH_3Cl; 2) CH_2Cl_2; 3) $CHCl_3$; 4) CCl_4.

It is known from the literature and from practical data that a number of difficulties arise in the industrial chlorination of methane due to complications connected with removal of heat and the necessity of having large cooling surfaces for complete condensation of the products when a considerable volume of gas is recirculated.

The chlorination products usually contain all four chloroderivatives of methane, and it is impossible in practice to carry out the reaction so as to produce only one of them.

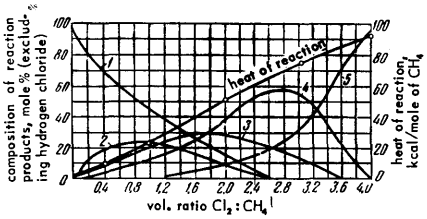


Fig. 3. Dependence of the composition of the chlorination products of methane and the heat of reaction on the volume ratio $Cl_2 : CH_4$. 1) CH_4; 2) CH_3Cl; 3) CH_2Cl_2; 4) $CHCl_3$; 5) CCl_4.

Fig. 2 shows that all ratios of chlorine to methane produce a mixture of chlorinated methanes, the methyl chloride content of which is greater as the proportion of methane in the feed mixture is increased[48].

Fig. 3, constructed from literature data, shows that evidently it is possible to obtain predominantly carbon tetrachloride if the molar ratio of chlorine to methane is greater than 3.0 : 1. Methylene chloride is produced industrially using a chlorine to methane ratio of 0.25–0.3 : 1; the heat of reaction in this case is 8 kcal/mole of methane (Fig. 3). When CCl_4 is produced, using a chlorine to methane ratio of, for instance, 3.5 : 1, the heat of reaction is more than 85 kcal/mole of methane.

Kiprianov and Kusner[49] have studied various methods for removing the heat evolved in the reaction and establishing standard conditions for the chlorination of methane to CCl_4. Dilution of the reacting gases with hydrogen chloride formed in the chlorination was the most effective.

The principle of recirculating the reacting gases in the chlorination of methane to maintain given temperature conditions has been employed in more recent years in a number of industrial establishments in the USSR, Germany, Italy, and other countries[50]. The recirculation of two-thirds of a reaction mixture consisting of 200 m^3 of CH_4 and 4.5 m^3 of Cl_2 at 350°–380° produces in 1 h 5 kg of CH_3Cl, 2.5 kg of CH_2Cl_2, 1 kg of $CHCl_3$, and 0.25 kg of CCl_4.[51]

The main requirement for the successful chlorination of hydrocarbons is the correct feed-rate and thorough mixing of the chlorine with the hydrocarbon, together with sufficiently effective removal of heat to avoid the explosive reaction

$$CH_4 + 2Cl_2 \rightarrow C + 4HCl.$$

Pease and Walz[33], Deanesly[34], Hass et al.[52], and Vaughan and Rust[10] have established that the thermal chlorination of lower paraffins begins only from 250° upwards. To obtain the maximum yield of methyl chloride a considerable excess of methane over chlorine and a fairly high temperature are required, while the production of carbon tetrachloride requires excess chlorine and the presence of active catalysts[53–58].

If chlorine is introduced into the reactor so that there is always an excess of methane or its partial chlorination products, mixtures can be obtained which contain from 90% methyl chloride to 100% carbon tetrachloride[55]. The optimum chlorination temperature is 400°–440°. In all cases 93–96% of the chlorine is converted.

Methane is chlorinated in Germany on a large scale to produce methyl chloride and methylene chloride[59]. One mole of chlorine is mixed with five moles of 99.5% methane and the mixture passed into a large internally cemented reactor externally heated to 390°–410°. The condensate consists of 50% of methyl chloride, 35% of methylene chloride, and 15% of higher chlorinated products. To obtain methylene chloride as the main product, the methyl chloride is returned to the reactor with the original gas mixture, in amounts up to 20% of the total gas feed.

For the chlorination of methane Wilson and Howland[48] used natural gas (2.5% C_2H_6, 88.5% CH_4, 9% N_2) or a gas containing 87.4% CH_4, 4.1% CO_2, 0.2% CO, 2.5% O_2, and 5.8% N_2. With a methane feed-rate of 150 litres/h, a temperature of 400°–440°, and chlorine to methane ratios of 0.37–2.02, the yield was 92.5–98.8% with respect to chlorine. The gas mixture contained 41.2–48.0% of chlorinated methanes and 49.6–52.8% HCl. On separating the chloromethanes, they were shown to consist of 16.9–61.0% CH_3Cl, 32.2–44.8% CH_2Cl_2, 7.6–36% $CHCl_3$, and 4.6–13.9% CCl_4. The quantity of carbon obtained was 0.038–0.121 g/h. With feed rates of 150 litres/h of CH_4 and 17 litres/h of Cl_2 at 440° and a nozzle diameter of 1.06 mm, a yellow flame was observed at the point of entry of the mixture, and carbon separated. With a feed rate of 75 litres/h of Cl_2 and a nozzle diameter of 2.5 cm a red glow appeared, with much formation of soot. With chlorine to methane ratios of 0.1, 0.3, 0.5, and 0.65, the amounts of carbon which separated were 2, ~3, ~8.0, and ~25 mg/h respectively.

A method has been described for the preparation of chlorinated methanes and hydrogen chloride by chlorinating the methane–hydrogen mixture obtained as a by-product in the cracking of kerosine[60]. The process is carried out in three tubes connected in series, 2 m high and 5 cm in diameter, each containing a layer of sand kept in turbulent motion. The methane–hydrogen mixture (40.5% H_2) is fed in at a rate of 370 litres/h, and the chlorine is fed into the three tubes at rates of 215, 403, and 277 litres/h respectively, the temperatures in the tubes being maintained at 350°, 360°, and 413°. Before condensation, the exit gas contained 1.3% of chlorine and 83% HCl. The residual gas contained 8.5% of the starting methane–hydrogen mixture. 99% of the methane fed was found in the chloromethanes and the residual gas.

A Japanese Patent[61] has described a method for the manufacture of lower chlorinated hydrocarbons and carbon tetrachloride. Aliphatic hydrocarbons are treated with 1.2–5 moles of Cl_2 and 1 mole of gaseous HCl at high temperature. At 500°–700°, a mixture of 1 mole of CH_4, 2 moles of Cl_2, and 1 mole of HCl gave 0.23 mole of CH_3Cl, 0.2 mole of CH_2Cl_2, 0.11 mole of $CHCl_3$, and 0.01 mole of CCl_4; 0.45 mole of CH_4 was recovered.

Stegner, Marczewska, and Treszczanowicz[62] carried out a series of experiments designed to increase the yield of CCl_4. The chlorination was carried out without a catalyst at 390°–400° with a methane to chlorine ratio of 5–6 in a mild steel reactor faced with bentonite. It was shown that the CCl_4 content of the reaction product could be increased to 50% by raising the reaction temperature to 420°–440° and the condensation temperature to 20°, but the C_2Cl_6 content also increased greatly; the vapour condensation temperature should be kept below 7°–10° to avoid large wastage of CH_4 and Cl_2 on side reactions, even though the CCl_4 content does not then exceed 20–30%. Best results were obtained by adding a 1 : 1 mixture of CH_2Cl_2

and $CHCl_3$ to the circulating gas; at a reaction temperature of 435° and a condensation temperature of 13°, a product containing 65% CCl_4 was obtained.

Developments in the industrial production of chloroform and carbon tetrachloride include the use of a two-stage process[63], comprising the gas-phase chlorination of methane to produce predominantly methylene chloride, and the liquid-phase photochemical chlorination of the latter to chloroform and carbon tetrachloride.

The thermal chlorination of methane to obtain tetrachloroethylene[64-67] and carbon tetrachloride is today of great importance. Thus 1 mole of CH_4 and 5 moles of Cl_2 are mixed with 9 moles of hot CCl_4 and the mixture passed into a reactor at 500°–700° to produce 96% C_2Cl_4.[64] Ethane or propane may be used instead of methane.

Chlorination on a fluidised-bed heat exchanger merits attention as a method for removing the heat of reaction and creating conditions which ensure thorough chlorination of methane, with CCl_4 as the main product.

In chlorinating a mixture of methane and hydrogen to give chloroform and carbon tetrachloride as the main products, Johnson[68] used a finely ground fluidised inert material in three series-connected reactors, without recirculation. Choporov and Tishchenko[23] showed that it is possible to chlorinate methane to produce CCl_4 as the main product by using as cooling agent a chemically inert granulated moving heat carrier at 390°–500°, with a molar ratio of chlorine to methane of 2.6–3.6 : 1. The reaction product contained the three higher chlorinated methanes, the contents of which could be changed within wide limits by regulating the reactant ratio. Increasing the chlorine to methane ratio within the above limits reduces the methylene chloride content of the product from 11.0 to 6.0% and the chloroform content from 40.4 to 24.5%, the carbon tetrachloride content increasing from 42 to 64%. With increase of the chlorine to methane ratio, the amount of unreacted chlorine rises from 2.7 to 8.0%, and the amount of chlorine required to produce 1 g of product rises from 2.8 to 3.2 g, the reaction temperature being 460°–480°.

Viriot[69] proposed the use of a special apparatus and a molar ratio $Cl_2 : CH_4 + CH_3Cl$ below 0.5. Brown, Colton, and Landau[70] chlorinated C_1–C_4 hydrocarbons at 500°–700°; for instance $1CH_4 + 3Cl_2 \rightarrow 4HCl + 0.48\ C_2Cl_4$; $1C_2H_6 + 5Cl_2 \rightarrow 6HCl + 0.94\ C_2Cl_4$.

Foster and Frankish[71] recommend the production of polychloromethanes by causing a mixture of Cl_2 with CH_3Cl, CH_2Cl_2, and $CHCl_3$ vapour in the molar ratio chloromethane : chlorine = 0.9–4 : 1 (the presence of CH_2Cl_2 is not essential) to come into contact with finely ground (50–100 mesh) inert material in turbulent flow at 250°–390°. Separation of the chloromethanes gave 3.5% CH_3Cl, 21.5% CH_2Cl_2, 51.0% $CHCl_3$, 23.0% CCl_4, and 1% of high-boiling product.

Chlorination of methane in the USSR[72]. Thermal chlorination is carried out on a large scale in the USSR. In the thermal process, destructive chlorination takes place, in addition to the formation of the chlorinated methanes, $CH_4 + 2Cl_2 = C + 4HCl$; as experience has shown, this reaction becomes noticeable at temperatures above 570° (with a methane to chlorine ratio of 3 : 1). In deciding on the chlorination conditions and the construction of the chlorinator, much attention is given to reducing side reactions to a minimum. The methane–hydrogen fraction, which is the waste gas from the separation of pyrolysis gas is used as raw material. Its composition is methane 72, hydrogen 23, ethylene 2, carbon dioxide 0.5, oxygen 0.5, and nitrogen 2.0 vol.%.

The technological process is as follows. Chlorine, mixed with the methane–hydrogen fraction in the ratio 1 : 3, is fed to the chlorinator, where the temperature is maintained at 500°–520° by the exothermic nature of the reaction. The temperature is regulated by changing the proportions of the gases fed to the reactor. The reaction mixture, containing chloromethanes, 25% of hydrogen chloride, excess methane, hydrogen, and nitrogen, is freed from hydrogen chloride, given an alkaline purification, and dried with a calcium chloride solution cooled to -15° with boiling ammonia. Before drying, the neutralised gas has the following composition: methyl chloride 10–12, methylene chloride 6–7, chloroform 1.5–2, residue (as carbon tetrachloride) 0.1, and methane + hydrogen + nitrogen 80 vol.%.

On drying, part of the chlorinated products is condensed and separated from the mixture. This portion of the products has the composition: methyl chloride 20, methylene chloride 50, chloroform 25, and carbon tetrachloride and other chlorides 5 vol.%. After being dried, the gases are compressed to 10 atm. and cooled to -40°; the main bulk of the chlorides condenses, the condensate containing 45 vol.% of methylene chloride, 13 vol.% of chloroform, and 2 vol.% of carbon tetrachloride and other chlorides. The excess of methane, containing a little methyl chloride, is recirculated to the chlorinator. The mixture of chlorides is rectified on three successive columns to separate methyl chloride (b.p. -23°), methylene chloride (b.p. 42°), and chloroform (b.p. 61.2°).

Production of methylene chloride in England[73] *. When methane separated from coke-oven gas is chlorinated methylene chloride is the main product, with chloroform and methyl chloride as by-products.

Unpurified coke-oven gas contains 15–15.2% H_2, 6–7% CO, 24–25% CH_4, 2–3% CO_2, 2–8% C_2H_6, and 10–12% N_2. After aqueous and alkaline purification and separation of hydrogen, 99.5% methane is obtained.

The chlorinator is a welded cylindrical pot lined internally with cement, 4580 mm high, with 1200 mm internal diameter, and 15 mm walls. The top 1 m is packed with 25 mm porcelain rings. In the centre of the pot is a cement tube 2400 mm long, into the top of which projects a nickel feed tube. 480 m^3 of chlorine and 240 m^3 of methane are fed per hour; the methane mixes with the circulating gas, which contains 20–25% N_2 and 5% CH_3Cl, the remainder being methane. The temperature is 410° above and below the chlorinator, and ~380°–400° in the centre. 53 000 m^3 of coke-oven gas per month are required for heating six reactors, or 13 m^3/h for one reactor. The reactor is shown in Fig. 4.

After cooling, the mixture of chlorides contains 48% CH_3Cl, 14% $CHCl_3$, 35% CH_2Cl_2, and 3% CCl_4. On rectification, CH_3Cl is obtained as final product (300–400 kg/h);

* This section is in fact a summary of a BIOS report[73] describing the chlorination of methane at the I.G. Höchst plant in Germany; the main product is methyl chloride. Some minor errors in the Russian text have been corrected to agree with the report[73] (Ed. of Translation).

TABLE 2. Raw materials, energy required, and yield of products per ton of methylene chloride.

Raw materials, source of energy, and products	Units	Per ton of CH_2Cl_2
Chorine	tons	4.08
Methane–hydrogen mixture	m^3	950
Electricol energy	kWh	1500
Steam	Mcal	6.20
Chloroform	tons	0.45
Hydrochloric acid, calculated as hydrogen chloride	tons	1.85

after removal of CH_3Cl, the chloride mixture contains 67–75% CH_2Cl_2 and 33–25% $CHCl_3$.

Preparation of methylene chloride in East Germany[74]. Methylene chloride is prepared technically by two methods: 1) thermal chlorination of methane with elementary chlorine; 2) esterification of methanol with hydrochloric acid and chlorination of the resulting methyl chloride with chlorine.

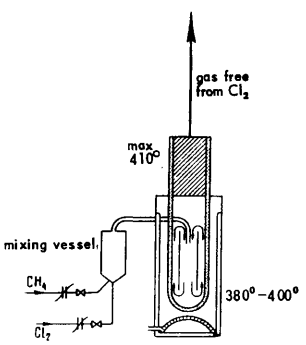


Fig. 4. The reactor.

For 30 years the first method has been that predominantly used in Germany. Methane from Ruhr gas is chlorinated to produce methyl chloride, methylene chloride, chloroform and carbon tetrachloride.

The electrochemical works at Bitterfeld uses the second method (Fig. 5), which is more profitable because of the smaller amounts of chlorine required. The chlorination of methane requires 2 moles of chlorine to produce 1 mole of CH_2Cl_2, $CH_4 + 2Cl_2 = CH_2Cl_2 + 2HCl$, while starting from methanol only one mole is required:

$$CH_3OH + HCl = CH_3Cl + H_2O,$$

$$CH_3Cl + Cl_2 = CH_2Cl_2 + HCl.$$

The resulting hydrogen chloride may be utilised for the first step. Here again the chlorination does not stop at the formation of methylene chloride; chloroform and a small amount of carbon tetrachloride are also formed.

A similar reaction starting from ethanol produces 1,1-dichloroethane, 1,1,1-trichloroethane, and 1,1,2-trichloroethane[75].

The Bitterfeld electrochemical works has developed and tested on a pilot-plant scale two methods for utilising the chloroform. The first is its chlorination to carbon tetrachloride, which is conveniently carried out in the liquid phase[76], and the other possibility is the reduction of chloroform to methylene chloride.

An adiabatic method has been proposed[77] for the chlorination of CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, or their mixtures, which may contain inert gases, below the decomposition temperature of the chlorination products.

The starting mixture and the reaction products, with a final temperature of 380°–420°, are fed through a cylindrical nozzle into the reactor in a volume ratio of more than 3 : 1 ("circulation coefficient"). Chlorine reacts almost quantitatively, any residue of it reacting in an auxiliary chamber (inside or outside the reactor), so that the exit gases contain less than 0.05% Cl_2. The starting gas may be fed to the reactor at a temperature between -20° and +320°. The reactor and other parts of the apparatus which come into contact with the reaction mixture are made of nickel or high-nickel steel. Before commencing the reaction, the reactor is heated to the initial reaction temperature, the hot circulation gas containing CH_4 or its chlorinated derivatives being passed through it at the same time. When the initial reaction temperature is reached the feeding of chlorine is commenced. With a mixture containing 18 vol.% Cl_2, 56.8 vol.% CH_4, 7.9 vol.% CH_3Cl, 0.4 vol.% CH_2Cl_2, and 16.9 vol.% of inert gas (temperature at the reactor inlet 15°, circulation coefficient 5 : 1), the reaction product contains 20.3 vol.% CH_3Cl, 52.5 vol.% CH_2Cl_2, 26.1 vol.% $CHCl_3$, and 1.1 vol.% CCl_4; with a mixture containing 9.2 vol.% Cl_2, 67.2 vol.% CH_4, 9 vol.% CH_3Cl, 0.3 vol.% CH_2Cl_2, and 14.3 vol.% of inert gas (temperature at the reactor inlet 190°, circulation coefficient 5 : 1), the product contains 25.2 vol.% CH_3Cl, 58.4 vol.% CH_2Cl_2, and 16 vol.% $CHCl_3$.

This method of chlorination has the following advantages. The absence of external heating of the reactor prevents the deposition of carbon on the walls. Since the reaction is independent of external heating, the reactor may be enlarged to any dimensions. The possibility of regulating the circulation coefficient ensures the maximum utilisation

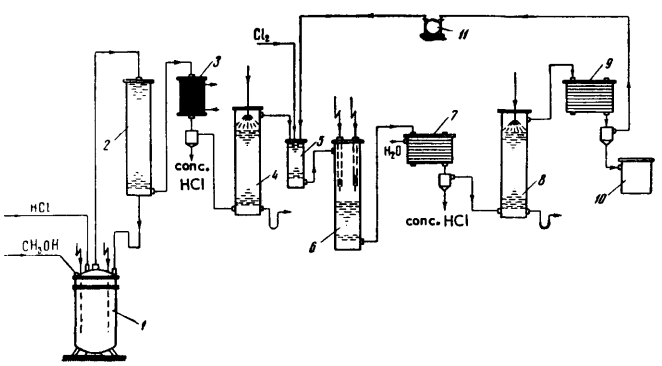


Fig. 5. Production of methylene chloride at the Bitterfeld electrochemical works.
1) Hydrochlorinator supply vessel; 2) hydrochlorinator; 3) condenser; 4) scrubber; 5) mixing vessel; 6) chlorinator; 7) HCl absorber; 8) scrubber; 9) low-temperature condenser; 10) receiver for crude product; 11) pump for gas recycle.

of the heat of reaction: thus with a circulation coefficient of 5 : 1, 83.3% of the heat of reaction is transmitted to the fresh gas, only 16.7% being carried away by the reaction products.

The results of works studies on the production of chloromethanes by the direct chlorination of natural gas have been published[78]. The natural gas is mixed with Cl_2 to give a molar ratio $Cl_2 : CH_4 = 0.2-0.5$, and the mixture fed to an externally heated reaction chamber, where chlorination takes place at 400°–420°, giving a mixture of all the chlorinated methanes.

A new process for the production of carbon tetrachloride. Carbon tetrachloride has usually been prepared by the action of elementary chlorine on carbon disulphide[78,79], but this process has recently been replaced by the thermal or photochemical chlorination of methane[80]. The thermal chlorination of methane developed in Rumania has been described[81]. High-purity natural gas and electrolytic chlorine are reacted in a cast iron vessel lined inside with acid-resistant cement with a high content of finely ground quartz.

The temperature in the reactor is held at 380°–400°. The reaction product contains 0.020 mole CH_4, 0.1410 mole $CHCl_3$, 0.9369 mole CCl_4, and 4.1671 moles HCl. The yield of chlorinated products is 95% based on chlorine. The chlorine is completely utilised, and the gases after scrubbing contain only 1.5–2.5% of methane.

The same process may be used to produce other chlorination products, such as methylene chloride and tetrachloroethylene, in high yield.

2) Thermal Chlorination of Ethane

The chlorination of the other gaseous paraffins (ethane, propane, and the butanes) has been much less studied than that of methane.

The thermal chlorination of ethane, which takes place at 600°, has also been used industrially[59]. The following processes occur:

a) $C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$,

b) $C_2H_6 + 2Cl_2 \rightarrow C_2H_4Cl_2 + 2HCl$,

c) $C_2H_5Cl \rightleftharpoons C_2H_4 + HCl$,

d) $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$.

In spite of the side reactions, the main product is ethyl chloride. Small amounts of vinyl chloride are formed by the pyrolysis of the dichloroethane. Ethane is chlorinated so much more easily than methane that it is possible to chlorinate it in a mixture of 10% ethane and 90% methane without substantial formation of chloromethanes[82].

Vaughan and Rust have studied the thermal and partial catalytic chlorination of ethane[83,84].

An American patent[85] describes the chlorination of hydrocarbons containing 2–6 carbon atoms by a two-stage process. The first stage comprises the simultaneous metaleptic chlorination of the hydrocarbon or partially halogenated hydrocarbon and the pyrolytic decomposition of the halogen derivative. The quantities of reactants may be so chosen that the products from the first stage are the starting materials for the second stage. Thus the addition of chlorine to acetylene produces tetrachloroethane, which is mixed with chlorine and ethane and used as starting material for the production of tetrachloroethylene and trichloroethylene in the first stage; part of the tetrachloroethylene and trichloroethylene is converted to pentachloroethane and hexachloroethane in the second stage.

The chlorination or bromination of ethane and higher paraffins is carried out in a vertical tube heated to 350° and filled with sodium chloride and/or bromide[86]; a mixture of SO_3 and the hydrocarbon is passed continuously into the tube. In this way ethane gave 1-chloro-2-bromoethane and 1-chloro-1-bromoethane. In a similar reaction using only NaBr at 300°–325°, ~91% of ethyl bromide was obtained.

3) Thermal Chlorination of Propane and Other Saturated Hydrocarbons

Propane is chlorinated more easily than methane and ethane, forming mono- and polychlorides.

Studies of the chlorination of propane confirm Hass's rules, according to which the rates of substituting hydrogen by chlorine at 300° on primary, secondary, and tertiary carbon atoms are in the ratio 1.00 : 3.25 : 4.43. When 2 moles of propane are chlorinated with 1 mole of chlorine the latter reacts completely to give a fraction containing 52.4% of 2-chloropropane and 47.6% of 1-chloropropane. Propane contains 6 hydrogen atoms attached to primary carbon atoms and 2 attached to the secondary carbon atom; hence the ratio of 1-chloropropane to 2-chloropropane in the reaction product should be $\frac{6 \times 1.00}{2 \times 3.25}$, which corresponds to 48% of 1-chloropropane and 52% of 2-chloropropane. With a propane to chlorine ratio of 2 : 1, ~15% of polychlorides is formed; with a ratio of 8 : 1 the quantity of polychlorides falls to 5%; in both cases the relative proportions of the monochlorides remain the same. Further chlorination of the 1- and 2-chloropropanes produces a mixture of 1,1-, 1,2-, 1,3-, and 2,2-dichloropropanes. From 1,3-dichloropropane, the important anaesthetic cyclopropane can be obtained; previously it had been prepared from trimethyleneglycol[59].

Mason and Wheeler studied the purely thermal chlorination of propane, using an excess of the hydrocarbon over the chlorine, high temperatures, and high linear velocities of the reactants[53]; under these conditions the degree of chlorination can be limited to produce monochloride as the main product.

Fruhwirth[87] produced a mixture of perchloroethylene and carbon tetrachloride by chlorinating hydrocarbons. A mixture of gaseous aliphatic hydrocarbons containing more than 2 carbon atoms (excluding C_4), or the corresponding halogen derivatives, was treated at 300°–800° (preferably 500°–600°) with approximately the theoretical amount of chlorine; when the starting hydrocarbon mixture contained an odd number of carbon atoms a mixture of perchloroethylene and carbon tetrachloride was obtained in 92% yield. The starting material may be propane, a mixture of propane, propylene, butane and isobutane, or a mixture of methylpentane, hexane and methylcyclopentane.

Krentsel', Topchiev, and Il'ina[19] studied the chlorination of propane in a continuous system with the molar ratio $C_3H_8 : Cl_2 = 1 : 2$ and space velocity 30 h^{-1}. Chlorination commences at 180°; as the temperature is increased, the conversion of chlorine also increases, this being more rapid in a tube filled with pieces of glass rod than in an empty reaction tube due to the chain nature of the reaction.

TABLE 3.

Temp., °C	Duration, min	Molar ratio $C_3H_8 : Cl_2$	Space velocity, h^{-1}	Composition of product, wt.%		
				mono-chlorides	di-chlorides	tri-chlorides
310	265	0.94:1	46	48.2	41.0	10.8
315	220	0.80:1	75	34.0	55.0	11.0
314	730	1:1	11	51.7	41.0	7.3
314	410	0.95:1	42	47.9	40.5	11.6
310	348	3.80:1	85	89.0	11.0	—
310	600	3.90:1	28	84.7	15.3	—
310	300	1.39:1	57	69.5	24.7	5.8
317	360	1.47:1	28	69.6	26.9	3.5
320	340	1.46:1	37	53.5	38.4	8.1

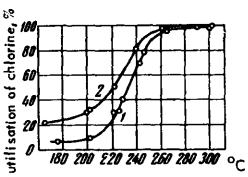


Fig. 6. Utilisation of chlorine as a function of temperature. 1) Empty tube; 2) packed tube.

The results of this study are given in Table 3. It is seen that altering the space velocity within the limits studied has little effect on the relative proportions of the various chloropropanes obtained.

Fig. 6 shows that in the thermal chlorination of propane the chlorine is completely utilised at 300°; changing the space velocity within the limits 11–85 h^{-1} has little influence on the composition of the chlorination products. With the ratio $C_3H_8 : Cl_2 = 4:1$ the relative proportions of mono- to dichloropropanes are almost independent of temperature; the reaction product contains 81.2 to 83.9% of monochloropropanes (comprising 57.2% of 1-chloro- and 42.8% of 2-chloropropane) and 16.1–18.8% of dichloropropanes (containing all possible isomers). With the ratio $C_3H_8 : Cl_2 = 2:1$ increase of the reaction temperature from 310° to 398° increases the dichloropropane content from 20.2 to 34.3% and the trichloropropane content from 1.5 to 7.7%. Fig. 7 shows the influence of the propane to chlorine ratio on the composition of the reaction products. Increasing the molar excess of the hydrocarbon in the reaction mixture causes a decrease in the yield of di- and trichloropropanes (Fig. 7).

Topchiev and Krentsel'[88] chlorinated propane in a small-scale apparatus[23], with mullite as a fluidised-bed heat exchanger. The starting propane contained 95.3 wt.% C_3H_8, ~4.2 wt.% C_2H_6, and ~0.5 wt.% C_4H_{10}. The experiments were carried out at 360°–395° with a space velocity of 60–180 h^{-1}. It was found that changing the chlorine to propane ratio from 1.58 to 2.1 leads to a slight decrease in the yield of di- and trichloropropanes and an increase in the yield of polychloropropanes; further increasing the ratio to 2.38 at sufficiently high space velocities causes an increase in the yield of di- and trichloro derivatives to 80–81%, as against 68–73% with a chlorine to propane ratio of 2.1. Only a small quantity of monochloropropanes is formed (1–4%), and this remains almost constant as the chlorine to propane ratio is increased from 1.58 to 2.38. On distilling the separate fractions, 1,1- and 1,2-dichloropropanes, 1,1,2- and 1,2,3-trichloropropanes, and 1,1,1,2- and 1,1,2,2-tetrachloropropanes are obtained.

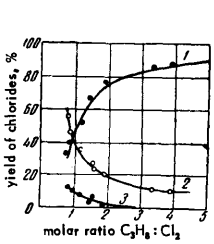


Fig. 7. Influence of the $C_3H_8 : Cl_2$ ratio on the composition of the reaction products. 1) Monochlorides; 2) dichlorides; 3) trichlorides.

The experiments on the extensive chlorination of propane on a fluidised-bed heat exchanger have shown that this process may be used to produce more highly chlorinated propanes and for the destructive chlorination of the reaction products to obtain carbon tetrachloride and perchloroethylene.

According to the German Federal Republic Patent 946,891[89] chlorinated derivatives are obtained by chlorinating saturated, unsaturated, or chlorinated hydrocarbons containing not less than two carbon atoms. Thus a mixture of 9 vol.% Cl_2 and 91 vol.% of propane at an initial temperature of 250° and the reaction chamber at 360° gives a chlorinated product containing 18.2 wt.% of isopropyl chloride, 34.6 wt.% of *n*-propyl chloride, 43.2 wt.% of 1,2-dichloropropane, and 4.0 wt.% of 1,2,3-trichloropropane.

Krentsel' and Pokatilo[90] studied the thermal chlorination of *n*-butane as the first step in the production of butyl alcohols by way of monochlorobutanes. They used 98–98.5% *n*-butane obtained by rectifying technical butane-isobutane fractions. From many experiments they showed that *n*-butane is chlorinated with 100% utilisation of chlorine at temperatures above 250°, and that filling the reaction tube with glass packing lowers the temperature at which chlorination commences, but does not lower the temperature at which there is complete utilisation of the chlorine. Monochlorides are obtained at space velocities of up to 500 h^{-1} with a 4.5 fold molar excess of butane in the reaction mixture. With a smaller excess of the hydrocarbon the yield of monochlorides does not exceed 80% at any space velocity. The monochlorides obtained contained ~60% of s-butyl chloride and ~40% of *n*-butyl chloride. At 400° the 1-chlorobutane content increases to 50%.

Topchiev, Andreev, and Krentsel'[91] carried out a series of experiments on the thermal chlorination of an isobutane fraction containing 66.5 vol.% of isobutane, 25.8 vol.% of *n*-butane, 5.8 vol.% of butylene, 0.9 vol.% of propane, 0.6 vol.% of isopentane, 0.3 vol.% of *n*-pentane, and a residue of 0.1 vol.%. 100% utilisation of chlorine with this fraction occurs at the same temperatures as with *n*-butane, but there is a higher yield of polychlorides at the same hydrocarbon to chlorine ratios. Chlorination of *n*-butane with a four-fold excess of hydrocarbon gives 100% yield of monochlorides, but in the case of isobutane, even with a greater hydrocarbon to chlorine ratio, the yield of monochlorides is only ~94%.

Topchiev, Krentsel', and Andreev[92] calculated from experimental data the energy of activation for the chlorination of the isobutane fraction to be 20000 cal/mole, and for the chlorination of *n*-butane under the same conditions, 39000 cal/mole. This might explain the higher yield of polychlorides in the chlorination of isobutane.

Nametkin and Serebrennikova[93] carried out experimental studies on the chlorination of alkanes as the first stage in

the production of alcohols. An interesting method for the thermal vapour-phase chlorination of *n*-pentane and isopentane to amyl chlorides is described by Ayres[94] and Clark[95].

Koch, Stallkamp, and Burrel[96], Dobryanskii and Gurevich[97], and Lemke and Tishchenko[98] chlorinated *n*-pentane in the vapour and liquid phase to obtain dichlorides. Dobryanskii and Gurevich[97] showed that vapour-phase chlorination is preferable for the synthesis of monochlorides.

Davydova, Papkina, and Tishchenko[99] were the first to chlorinate synthetic isopentane in the liquid phase at 18°–−20° and in the vapour phase in the apparatus described by Kursanov[100]. With 2 moles of chlorine and 1 mole of isopentane, the reaction product contained ~30% of monochlorides, 60% of dichlorides, and 10% of trichlorides. 2,3-dichloro-2-methylbutane, 2,4-dichloro-2-methylbutane, and 1,4-dichloro-2-methylbutane were found in the products.

Markovnikov[6], who chlorinated *n*-hexane in an atmosphere of dry and of moist chlorine, showed that the best yield of monochloride is obtained with moist chlorine.

Studies on the chlorination of hexanes have not fully revealed conditions for obtaining monochlorides as the main product with complete utilisation of the chlorine.

Galanina[101], continuing the work of Nametkin and Serebrennikova[93], chlorinated *n*-hexane from petroleum. She achieved complete utilisation of chlorine with a maximum yield of monochloride at 235°, with the ratio $C_6H_{14}:Cl_2$ = = 10:1 and space velocity 0.73 litre/h per litre of reactor volume. Higher temperatures did not give improved results, and a lower temperature gave a lower yield of monochloride. With hexane to chlorine ratios of 3:1 and 6:1, there were frequent flashes in the reactor, which caused local overheating and deposition of carbon on the walls. The monochloride was separated on a rectification column into a fraction of b.p. 122°–125°, corresponding to 2-chlorohexane, and a fraction of b.p. 134°–136°, corresponding to 1-chlorohexane. The resulting monochloride was again chlorinated, producing under certain conditions dichlorohexane in a yield of 98.7%.

Galanina and Nekrasov[27] chlorinated *n*-heptane in the vapour phase at high temperature in an attempt to attain the maximum yield of monochloride with complete utilisation of the reacting chlorine. The chlorine was in excess. The monochloride which formed was immediately removed from the reaction zone. Their experiments showed that increase of temperature increases the yield of monochloride, and that the chlorine reacts completely to give monochloride in 96.5% yield at 260°, with space velocity 0.72* and reactant ratio 10:1.

McBee and Hass[102] chlorinated propane, *n*-butane, isobutane, *n*-pentane, isopentane, and *n*-heptane at atmospheric pressure. They established the following rules.

1) If an aliphatic hydrocarbon is chlorinated at an elevated temperature or under the influence of light, all the isomers theoretically possible are formed.
2) At low temperatures hydrogen atoms attached to secondary and tertiary carbon atoms are substituted more rapidly than those on primary carbon atoms.
3) At 600° and above the chlorination is not selective, and all hydrogen atoms are substituted at the same rate; under these conditions the yield of primary isomers is ~90 vol.% of the total monochlorides in the case of isobutane, 60 vol.% in the case of *n*-butane, and 75 vol.% in the case of propane.

McBee, Hass, and coworkers[103] studied the thermal chlorination of hydrocarbons in the vapour phase under pressure and at an elevated temperature. At 500° and 500 atm with a large excess of chlorine, pentane gave 90% of the theoretical quantity of CCl_4 and 10% of hexachloroethane. At 300°–360° and 100 atm hexane or octane produced CCl_4 and hexachlorobutadiene. There was no deposition of carbon.

Nekrasova and Shuikin[104] studied the possible thermal chlorination of *n*-hexane, *n*-heptane, *n*-nonane, and *n*-decane, and established the optimum conditions and the main features of the process. The hydrocarbons were chlorinated thermally in the absence of light, when the reaction may be limited to the formation of primary or secondary monochlorides or dichlorides. A study of the way in which the temperature influenced the chlorination showed that for each of the hydrocarbons there are certain most favourable conditions for the formation of mono- and dichlorides. Thus the optimum temperature for the formation of 1-chlorohexane is 197°, for 1-chlorononane 317°, for 1-chloropentane 257°, for 1-chlorooctane 277°, and for 1-chlorodecane 357°. The optimum time of contact is 0.2 to 0.3 sec, and the optimum hydrocarbon to chlorine ratio from 6:1 to 10:1, depending on the hydrocarbon. The conditions for obtaining high yields of secondary alkyl chlorides were also established; the optimum temperatures are *n*-hexane 77°, *n*-heptane 137°, *n*-octane 177°, *n*-nonane 187°, and *n*-decane 197°. 1-Chlorohexane and 1-chloroheptane could be thermally chlorinated to produce the corresponding dichlorides in almost quantitative yield.

This study thus provides a method for synthesising chloroalkanes in simple and available apparatus, simply by altering the reaction conditions. The authors called this method directed thermal chlorination.

III. CATALYTIC CHLORINATION OF SATURATED HYDROCARBONS

Catalytic and photochemical chlorination have received much less attention than thermal chlorination, and most work in this field relates only to methane and ethane.

Catalytic chlorination has been studied with a view to the possible reduction of the chlorination temperature by using various solid catalysts. Up to the present, homogeneous catalysis in the chlorination of hydrocarbons has received little attention, although the use of homogeneous catalysts in radical reactions gives very interesting results, as Topchiev and Ananiya have shown[105].

It is known that various metal chlorides (ferric chloride, silver chloride, partially reduced cuprous chloride, aluminium chloride, manganous chloride, antimony pentachloride, and platinum, zinc, cadmium, tin and lead chlorides impregnated on carbon), and various adsorbent materials mixed with finely ground calcium oxide, may be used as catalysts[106-111].

The conditions for chlorinating paraffinic hydrocarbons to produce specified products depend not only on the nature of the catalyst, but also on the hydrocarbon to be chlorinated.

* Litre/h per litre of reactor volume. (Ed. of Translation)

No noticeable influence on the relative rates of substitution of hydrogen attached to primary and secondary carbon atoms in the photochemical chlorination of paraffins is shown by such catalysts as the chlorides of antimony, tin, aluminium, titanium, and bismuth, nor by iodine and sulphur.

1) Catalytic Chlorination of Methane

Among inorganic catalysts, cupric chloride has attracted most attention.

Boswell and McLaughlin[112] and Deanesly[109] have demonstrated the use of cupric chloride in the catalytic chlorination of methane to methyl chloride. This work has been confirmed and extended by Mamedaliev and his coworkers[113], who showed that in the preparation of methyl chloride from natural gas, best results are obtained with a catalyst of cupric chloride on pumice promoted with cerium chloride. Catalysts which have a high adsorptive capacity for chlorine are unsuitable for the production of methyl chloride, but favour the formation of more highly chlorinated products, particularly CCl_4, probably because the catalyst surface adsorbs chloromethanes to a greater extent than methane, thus producing more extensive chlorination[112-116].

Polanyi and Bogdandy have shown in their patent[117] that it is possible to obtain methyl chloride by adding small amounts of sodium, cadmium, or zinc vapour to the mixture of chlorine and methane, while Martin and Lux[118] have chlorinated methane in the presence of the vaporised lower chlorides of polyvalent elements which are capable of forming higher chlorides, for instance, antimony trichloride. Sper[119] has described the chlorination of saturated hydrocarbons (including methane) in a heated reaction chamber filled with graphite lumps. The use of catalysts in the chlorination of methane has also been discussed in several other papers[50].

The published data on the catalytic chlorination of methane lead to the conclusion that in order to obtain an optimum yield of CH_3Cl it is necessary to use a considerable excess of methane over chlorine and a fairly high temperature in the reaction tube (empty or filled with a porous material). To obtain CCl_4 it is necessary to have first of all an excess of chlorine over methane as well as active catalysts; the tendency of the reacting gases to explode is reduced by introducing gases such as carbon dioxide and nitrogen into the reaction zone. In the chlorination of methane the hydrogen chloride formed accounts for 50% of the reacting chlorine for each atom of chlorine which combines with methane; hence the search for new methods of chlorinating hydrocarbons with the minimum formation of hydrogen chloride is of theoretical and practical interest[120-122].

Chlorination in the presence of chlorine carriers (melts of certain, mainly copper, salts) can bring about oxidative chlorination of hydrocarbons, as well as the normal chlorination, with simultaneous utilisation of the hydrogen chloride[24].

$$RH + 2CuCl_2 \rightarrow RCl + Cu_2Cl_2 + HCl$$

$$Cu_2Cl_2 + 2HCl + \tfrac{1}{2}O_2 \rightarrow 2CuCl_2 + H_2O.$$

In this process the heat of chlorination is partly compensated by the endothermic regeneration of the cupric chloride, the temperature of the chlorination being thereby more easily controlled. Pure cupric chloride or a eutectic salt mixture, e.g $Cu_2Cl_2 + KCl + CuCl_2$, is used as chlorine carrier. The use of salt melts simplifies the removal of heat, but causes other difficulties, because of the necessity of circulating a melt at high temperature in the reaction system. Detailed studies of the kinetics of the chlorination of methane in the presence of salt melts have appeared in recent years[123].

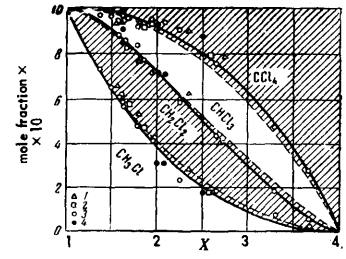


Fig. 8. Distribution of chlorinated methanes in the reaction product. X is the ratio of g-atoms of chlorine to moles of chlorinated product.
1) HCl - air - CH_4; 2) HCl - O_2 - steam - CH_4; 3) Cl_2 - - air - CH_4; 4) CH_4 - Cl_2.

Meisner and Thode[124] reported the existence of local overheating when a fixed catalyst (cupric chloride on pumice) is used for the chlorination of methane at 440°–550° in the presence of hydrogen chloride and oxygen. They carried out experiments on the oxidative chlorination of methane with the following systems: 1) HCl–air–methane; 2) HCl–oxygen–steam–methane; 3) chlorine–air–methane. Analysis of the experimental results showed that the reaction mixtures contain all four chloromethanes, but their proportions differ in the different systems (Fig. 8).

The same effect was noticed by Wilson and Howland[48], who showed that the variation in the proportions of the products in the different systems may be explained by equilibrium between CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 in accordance with the equations

$$CH_3Cl + CHCl_3 \rightleftharpoons 2CH_2Cl_2, \quad (1)$$

$$CH_2Cl_2 + CCl_4 \rightleftharpoons 2CHCl_3. \quad (2)$$

Meisner and Thode found that when chlorine is mixed with methane and air, its conversion by the reaction

$$2CH_4 + Cl_2 + \tfrac{1}{2}O_2 = 2CH_3Cl + H_2O$$

was 70–90%, and the conversion of hydrogen chloride by the reaction

$$CH_4 + HCl + \tfrac{1}{2}O_2 = CH_3Cl + H_2O$$

was 65–80%. 10–40% of the methane is converted, and, depending on the reaction conditions, 20–50% of the methane is burnt on the overheated parts of the catalyst, because of poor removal of heat from the reaction zone.

Soviet[24] and foreign[125] workers have shown that methane can be subjected to oxidative chlorination in a continuous system with a heterogeneous catalyst of a porous material. Under certain conditions CCl_4 can be obtained as the main product (up to 75% of the total chlorinated methanes).

Churchill and Thomas[125] prepared chlorinated hydrocarbons from organic compounds, particularly lower aliphatic alcohols, by using melts of NH_4Cl and chlorides, bromides, and fluorides of metals of Groups I and II of the Periodic System, e.g. Cu_2Cl_2, NaCl, $ZnCl_2$, and KCl, at 250°–500°. With a melt of Cu_2Cl_2, NH_4Cl, and $ZnCl_2$ the reactions were carried out at 335°–347°.

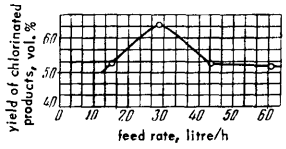


Fig. 9. Dependence of the yield of chloroderivatives on the rate of flow of the gas mixture. Temperature 460°; $CH_4 : O_2 : Cl_2 = 1 : 0.175 : 0.240$.

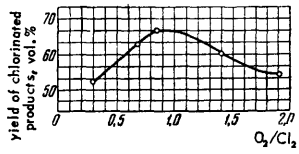


Fig. 10. Dependence of the yield of chloroderivatives on the oxygen to chlorine ratio. Temperature 460°; rate of flow of gas 30 litre /h.

Corin[126] showed that $HgCl_2$ may also be used as the chlorine carrier, the reaction being carried out in the vapour phase at 500°–650° in accordance with the equation

$$HgCl_2 + CH_4 \rightarrow CH_3Cl + HCl + Hg.$$

Vdovichenko, Galenko, and Sarishvili[25] studied the possibility of direct oxidative chlorination of natural gas in a melt of KCl and $ZnCl_2$ containing $CuCl_2$ as catalyst; the studies were made on methane–oxygen–chlorine and methane–air–chlorine gas mixtures.

The experiments showed that the content of unreacted chlorine in the exit gases decreases from 2.5 vol.% at 360° to 0 vol.% at 500°. The optimum reaction temperature is 450°; at lower temperatures the yield of chlorinated products decreases because of the larger amount of unreacted chlorine in the reaction products, and at higher temperatures the yield falls because of destructive chlorination of the methane to hydrogen chloride and soot, which can be observed visually. The maximum yield of chlorinated methanes is obtained with a reactant feed rate of ~30 litres/h (Fig. 9). At 460° and a feed rate of 30 litres/h, the yield of chlorinated derivatives reaches 60–68% with an oxygen to chlorine ratio of 0.68–0.85 (Fig. 10). Thus in the oxidative chlorination of methane in a $KCl–ZnCl_2–CuCl_2$ melt under optimum conditions, the yield of chloromethanes, calculated with respect to chlorine, reaches 60–64%, which is 11–15% greater than the yield obtained in the vapour-phase thermal (non-oxidative) chlorination.

In the direct oxidative chlorination of methane in a $KCl–ZnCl_2–CuCl_2$ melt, the resulting chloromethanes contain 85–90 mole % of methyl chloride, 9–14 mole % of methylene chloride, 2–5 mole % of chloroform, and up to 1 mole % of carbon tetrachloride.

Bijawat, Patel, and Potnis[127] have described the application of a fluidised-bed catalyst for the chlorination of methane. They used activated carbon, pumice, and copper chloride on pumice, comparing their activity with that of sand as an inert material. The methane contained 90% CH_4, 9.4% CO_2, 0.2% CO, and traces of H_2 and N_2; O_2 was absent. Carbon tetrachloride was obtained as the product. The apparatus used is shown in Fig. 11. The experiments were carried out with a chlorine to methane ratio of 4 : 1, a rate of chlorine feed of 0.5–2.2 moles/h, and reaction temperature 250°–500°.

At all feed rates, the yield of CCl_4 rose to a maximum as the temperature increased, and then fell (Fig. 12). The highest yield of CCl_4 was obtained with activated carbon as catalyst, and the lowest with sand. The yield was 90% of the theoretical calculated with respect to chlorine (Fig. 13).

Mickley and Trilling[128] found that the heat transfer coefficient in fluidised layers is 3–70 times as much as in empty tubes. Gilliland and Mason[129] assert that, because of heat transfer by the solid particles, a comparatively homogeneous temperature is maintained in a fluidised layer throughout its volume, in spite of the large variations in the

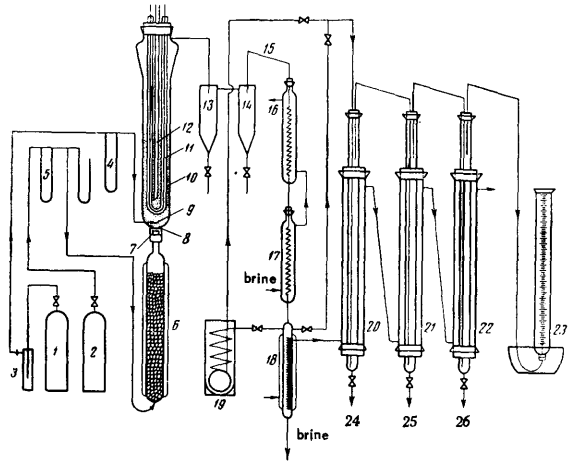


Fig. 11. Apparatus for the chlorination of methane: 1), 2) gas cylinders; 3) sulphuric-acid bottle; 4) manometer for methane; 5) manometer for chlorine; 6) preheater; 7), 12) Chromel-Alumel thermocouple; 8) distribution plate; 9) inlet pipe 2.5 cm above the distribution plate, fixed to the bottom of the reactor; 10) reactor with fluidised layer; 11) internal nichrome wire heater; 13) dust trap; 14) cyclone; 15) air condenser; 16), 17) spiral condensers; 18) straight tube condenser; 19) additional condenser; 20), 21), 22) absorbers; 23) graduated cylinder; 24)-26) valves for the removal of the chloromethanes.

heat liberated at different heights; hence it would appear that a reactor with a fluidised layer is more suited to a chlorination reaction than is an empty tube or a fixed-bed reactor.

Pie[130] has patented an apparatus for the chlorination of methane in which the reagents are passed through a zone of gradually increasing catalytic activity; the inlet end of the reaction chamber is cooled, and the outlet end heated. It is asserted that this construction enables the reaction to be easily controlled without any sudden increases of temperature, while retaining a high reaction rate.

Methane can be chlorinated in the presence of CCl_4 at 345°–400° on a fluidised-bed catalyst with a gas flow of 6–30 cm/sec and a chlorine to methane ratio of 1 : 10; higher yields of chloroform and carbon tetrachloride are obtained[131].

Another patent[132] describes the preparation of CCl_4 and C_2Cl_4 in a combined yield of 90% at 300°–370° with a feed of 1 mole of CH_4 to 3.6–4 moles of Cl_2; the catalyst is an untreated material of low density, such as wood charcoal, silica gel, or Fuller's earth.

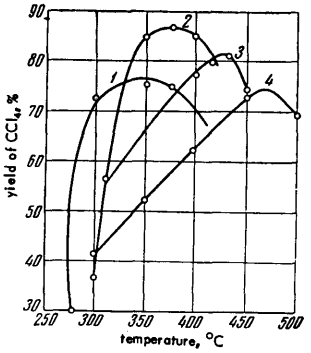


Fig. 12. Influence of temperature and rate of chlorine feed on the yield of CCl_4. activated carbon as the fluidised solid. Rate of chlorine feed, moles/h: 1) 1.01; 2) 1.31; 3) 1.93; 4) 3.20.

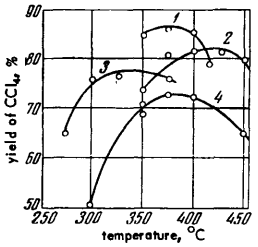


Fig. 13. Influence of the nature of the fluidised solid on the yield of CCl_4;
Fluidised solid; 1) activated carbon; 2) pumice; 3) cupric chloride on pumice; 4) sand.

Joseph and Pye[133] carry out the oxidative chlorination of hydrocarbons (e.g. methane and ethane) in a reaction chamber containing a carrier such as diatomaceous earth and copper chloride. Copper chloride is oxidised by air in the first zone to copper oxychloride, which is converted by HCl in the second zone to $CuCl_2$; this is reduced to CuCl by the hydrocarbon.

Kuntz, Cocherell, and Disberger[134] passed a mixture of CH_4 and Cl_2 (in molar ratio 1:3.6–1:4) through a reactor at 300°–370° over a fluidised-bed catalyst [wood charcoal, synthetic $Al_2(SiO_3)_3$, synthetic silica-alumina gel, silica gel, or Fuller's earth, 60–100 mesh] maintained in the fluidised state by the stream of gas, velocity 0.03–0.3 m/sec at the above temperature in an empty reactor. After separating the catalyst, the reaction products contained CCl_4 and C_2Cl_4.

Ketslakh, Rudkovskii, and Suknevich[135] prepared methylene chloride by chlorinating methane in glass tubes 60 mm long and 15 mm in diameter. The reaction space (50 cm^3) was filled with glass rings or $CaCl_2$, and the methane to chlorine ratio was 1:2. The yield of methylene chloride was practically constant over the temperature range 380°–450°. Chloroform and carbon tetrachloride are formed when the rate of flow of the gases is reduced. It was shown that it was best to use methane containing methyl chloride, the yield of methylene chloride then being 73.6% with respect to chlorine and 34% with respect to methane.

Iserson[136] prepared CCl_4 in 60–70% yield by reacting $COCl_2$ with PCl_5 at 350° under pressure with activated carbon as catalyst.

Thomas and Hundley[137] passed a mixture of 2.2 parts of CH_4 and 1 part of Cl_2 through a vertical reactor filled with glass beads and containing S_2Cl_2 at a rate of 45 g/h at 20°, and obtained 36 g of CH_3Cl per hour with traces of CH_2Cl_2. With the ratio $CH_4:Cl_2$ = 3.6:1 at 70° they obtained 215 g of CH_3Cl and 113 g of CH_2Cl_2 per hour. Methane conversion was 78%. 14 moles of $CHCl_3$ were obtained for 100 moles of CH_3Cl; CCl_4 was not formed. Methylene chloride may be prepared analogously from methyl chloride and chlorine[138].

2) Catalytic Chlorination of Ethane and Other Saturated Hydrocarbons

The catalytic chlorination of ethane and other saturated hydrocarbons has been less studied than that of methane.

Mamedaliev[113] obtained hexachloroethane in 70% yield by chlorinating ethane over activated carbon at 350°–400°. Foster[139] prepared ethyl chloride from 5 volumes of ethane and one volume of chlorine with a $CuCl_2$–Al_2O_3 catalyst at 450°–500° with a contact time of 0.3–0.5 sec, the yield being 80% with respect to chlorine.

Other workers[140] have chlorinated ethane in the vapour phase in the presence of suspended graphite powder; the composition of the chlorination product varied with the experimental conditions. With this catalyst at 400°, a contact time of 0.19 sec and gas feed of 7.6 g/h, Furr and Neher[141] obtained a product containing 0.4% CH_2 = CHCl, 60.29% C_2H_5Cl, 29.2% CH_3CHCl_2, and 6.4% CH_2ClCH_2Cl and $ClCH_2CHCl_2$. The degree of conversion of ethane to ethyl chloride reached 44%. The chlorination of 1,1-dichloroethane on graphite at 450° with a contact time of 8 sec gives trichloroethylene in 81.4 mole % yield[142].

McBee and Bittles[143] chlorinated ethane in the vapour phase in the presence of fluorine at room temperature or below in a current of nitrogen as diluent, and obtained ethyl chloride and dichloroethane in 90–100% yield with complete utilisation of the chlorine.

Topchiev, Krentsel', and Andreev[144] studied a number of heterogeneous catalysts for the chlorination of technical *n*-butane in a continuous system, and found an iron catalyst, which considerably lowered the apparent energy of activation, to be the most active. A high yield of polychlorinated derivatives was obtained with these catalysts, the yield of monochlorides not exceeding 50% of the total.

Krentsel', Topchiev, and Il'ina[145] studied the continuous chlorination of propane on silica gel impregnated with $CuCl_2$, an iron catalyst in the form of a spiral of stainless steel, and in the presence of oxides of nitrogen. They showed that the iron catalyst is the most effective, the chlorination commencing at a low temperature and more than 30% of the chlorine reacting at 40°. Under comparable conditions, the yield of di- and trichloro derivatives was considerably higher with the copper chloride impregnated silica gel than with the iron catalyst. The addition of 1–2% NO_2 has a strong catalytic effect, giving a higher chlorine utilisation than in the purely thermal process.

Topchiev and Alaniya[105] were the first to show that chlorine is a homogeneous catalyst for the nitration of hydrocarbons with oxides of nitrogen in the vapour phase; in addition to the nitrated hydrocarbons which are the main product, chlorides are also formed. This suggested that with certain proportions of chlorine and oxides of nitrogen it should be possible to direct the reaction so as to produce chlorides as the predominant product, thus using the nitrogen oxides as catalysts for the chlorination. To confirm this suggestion, butane was chlorinated in the usual continuous system with the addition of 2% NO_2 to the reaction

mixture; the chlorination commenced at a lower temperature, and at 150° the utilisation of chlorine reached 44%, while in the absence of NO_2 there is no reaction at all at this temperature.

The reaction of NO and Cl_2 with methane in the vapour phase from room temperature (25°–30°) to about 300° has also been studied, with the ratios $CH_4:NO = 4:1$ and $CH_4:Cl_2 = 1:3$. In addition to nitration and chlorination products, oxidation products of methane were also observed: small amounts of formaldehyde were detected in the gaseous products, and were absorbed in ammonia to form hexamethylenetetramine. Under identical conditions, there was no reaction between chlorine and methane in the absence of oxides of nitrogen, and no nitration of methane by nitrogen oxides in the absence of chlorine. Only the simultaneous action of chlorine and nitrogen oxides on methane at elevated temperatures can provide a series of products under fairly mild conditions.

Nekrasova and Shuikin[20] studied the reaction products in the vapour-phase (265°–400°) and liquid-phase (123°–213°) chlorination of *n*-alkanes from C_6H_{14} to $C_{12}H_{26}$ with a molar ratio of alkane to chlorine = 1:1, with 2% NO_2 as catalyst in the presence of 1% of unsaturated hydrocarbons as chain initiators. They also[21] studied the chlorination of *n*-dodecane in the vapour and liquid phases in the presence of NO_2, the use of which enables the reaction temperature to be lowered by 70°–100° and produces monochlorides in high yield.

Profft[146] carried out the simultaneous chlorination and nitration of propane and pentane. A stream of nitrogen was passed through the hydrocarbon, heated almost to boiling, and the hydrocarbon vapour mixed with HNO_3 vapour and N_2, and then with Cl_2, after which the mixture was heated to 240°–400°; in the case of pentane the final product contained 3.5% N and 31% Cl.

The catalytic action of small quantities of olefines on the chlorination of saturated hydrocarbons is of much interest.

Thus Stewart and Weidenbaum[147] showed, in agreement with Deanesly's patent[110], that the chlorination of pentane (and also propane and butane) is quite strongly accelerated in the presence of ethylene, and (significantly) practically no dichloroethane is formed. Stewart and Weidenbaum conclude that this "initiation" of the hydrocarbon chlorination is a chain process and suggest the following reaction mechanism:

1) $Cl_2 \rightarrow Cl\cdot + Cl\cdot$,

2) $C_2H_4 + Cl\cdot \rightarrow C_2H_4Cl\cdot$,

3) $C_2H_4Cl\cdot + C_5H_{12} \rightarrow C_2H_4 + C_5H_{i1} + HCl$,

4) $C_5H_{i1} + Cl_2 \rightarrow C_5H_{11}Cl + Cl\cdot$, etc.

They introduce the concept of the so-called "induction factor", which is the ratio of chlorine reacting by substitution to chlorine reacting by addition. From their earlier work on the photochemical chlorination of paraffins and olefines, they suggest that in thermal (mainly high temperature) chlorination in the presence of olefines, the atomic chlorine formed in the chain reaction reacts by two competing processes (shown as applied to ethylene):

1a) $Cl\cdot + Cl_2 \rightarrow Cl_3$,

1b) $Cl\cdot + C_2H_4 \rightarrow C_2H_4Cl\cdot$.

Assuming that the active chlorine molecule reacts predominantly by addition and the radical $C_2H_4Cl\cdot$ mainly by substitution, they suggest that the chain mechanism of the

TABLE 4.

Catalyst	Apparent energy of activation, cal/mole
None	39 000
Inert filler	17 000
Activated alumina	15 000
Silica gel	8 000
Silica gel + 20% $CuCl_2$	4 500
Iron catalyst	4 500

"induced" chlorination of, for example, pentane in the presence of ethylene may be represented as follows:

2) $C_2H_4 + Cl_3 \rightarrow C_2H_4Cl_3 \rightarrow C_2H_4Cl_2 + Cl\cdot$,

3a) $C_2H_4Cl\cdot + Cl_2 \rightarrow C_2H_4Cl_3 \rightarrow C_2H_4Cl_2 + Cl\cdot$,

3b) $C_2H_4Cl\cdot + C_5H_{12} \rightarrow C_2H_4 + C_5H_{i1} + HCl$,

4) $C_5H_{i1} + Cl_2 \rightarrow C_5H_{11}Cl + Cl\cdot$,

with corresponding steps for breaking the chains.

In more recent work, Rust and Vaughan[11] have investigated the inhibition by olefines of the substitution chlorination of paraffins and olefines at moderate temperatures (up to 200°); for example, at 135° substitution is markedly inhibited by the presence of 20% of propylene in the hydrocarbon mixture.

"Induced" chlorination and similar processes have been little studied.

Attention is drawn to papers and patents by Deanesly and his coworkers[109-111] relating to the chlorination of mixtures of paraffins and olefines.

IV. PHOTOCHEMICAL CHLORINATION

Photochemical chlorination, in which the absorption of a light quantum decomposes a molecule into two atoms or radicals, is of tremendous value in studying the theory of chain reactions.

Both liquid and gaseous hydrocarbons can be chlorinated photochemically; it is particularly convenient to chlorinate the former by passing chlorine through the liquid reaction mixture while stirring and irradiating with ultraviolet light.

Butlerov[148] chlorinated butane photochemically by mixing 10 volumes of the hydrocarbon with 9 volumes of chlorine in glass vessels in the dark, and submitting the mixture to the action of daylight; after several hours a large quantity of hydrogen chloride and a heavy oil were formed; the latter contained alkyl halides and a high proportion of higher chlorination products.

Tolloczko and Kling[149] demonstrated the influence of sunlight and light from a mercury-vapour lamp, and Bedford[150] that from an arc discharge, on the reaction between methane and chlorine.

Rollefson[151] states that the photochemical chlorination of paraffins leads to the successive substitution of two hydrogen atoms by chlorine, and is often accompanied by an explosion. However, according to Whiston[152], monochlorides can be obtained in good yields by photochlorination in diffuse sunlight or corresponding artificial light if the hydrocarbon to chlorine ratio is controlled[153].

When chlorinating gaseous hydrocarbons, it is recommended that the hydrocarbon and chlorine be introduced into a solvent inert to the action of chlorine and that the stirred solution be irradiated with ultra-violet light[44].

In spite of the large number of papers on the photochemical chlorination of paraffins, interest in this field has not decreased in recent times. Photochemical excitation is as yet little used in industry.

McBee and Pierse[154] chlorinated methane at 150°–450° under the influence of ultra-violet radiation with a contact time of 5 min, and obtained tetrachloroethylene (35% conversion) and carbon tetrachloride. In the industrial process methane is 80–90% converted into chlorinated products at 340°–370°; by adjusting the reaction conditions it is possible to obtain the final products in any desired proportions. The reaction of methane with chlorine at 315° in a tube filled with Fuller's earth produces 46% C_2Cl_4, 45% CCl_4, and 9% C_6Cl_6 and C_2Cl_6; the conversion is 67% (based on chlorine). The chlorination of ethane at 400° with a contact time of 0.19 sec produces 4% C_2H_3Cl, 60.2% C_2H_5Cl, 29.2% $CHCl_2CH_3$, 6.4% CH_2ClCH_2Cl, and 0.2% $CHCl_2CH_2Cl$; the overall conversion, based on ethane, is 81.2%. The chlorination of hexane at 97° with a contact time of 0.2–0.3 sec produces 67% of a mixture of primary and secondary chlorides. The chlorination of heptane at 157° gives 57% of secondary and 19% of primary chlorides; of octane at 177°, 66% and 32% respectively; of nonane at 187°, 65% and 3%; and of decane at 197°, 61% and 3%. It may be concluded that increasing the molecular weight of the hydrocarbon leads to a reduced selectivity and the formation of a larger amount of dichlorides.

Henning and Pessel[155] prepared CCl_4 by chlorinating $CHCl_3$, heated to nearly 61°, in the liquid phase in the presence of PCl_3 as catalyst under illumination. Chlorine was passed into the solution through a porous glass plate while illuminating the apparatus with two 100 W bulbs; the yield of CCl_4 was 90–95%, based on reacted $CHCl_3$, or 90% based on chlorine, with recycling of unreacted chlorine.

An autocatalytic photochlorination process has been described. A mixture of chlorine and hydrogen was burnt in a concentric tube at 250°–300°, and a 1 : 4 methane–chlorine mixture (20 g CH_4 + 80 g Cl_2 per hour) was simultaneously passed into the tube; in addition to hydrogen chloride 0.06 parts of a mixture of $CHCl_3$ and CCl_4 were obtained[156].

Skuters and Cooper[157] also prepared CCl_4 by the photochemical chlorination of methane by continuously introducing Cl_2 into a stream of liquid CH_4.

McBee, Hass, Burt, and Neher[158] chlorinated (by the photochemical method) ethane, saturated at 0° with lead tetraethyl, with a mixture of chlorine and nitrogen at 132°. The chlorine utilisation was 95%, and the product contained 80 mole % of ethyl chloride and 20 mole % of higher chlorides, mainly 1,1-dichloroethane. The products of the photochemical chlorination of ethane at 125°–150°, using a substantially equimolar proportion of chlorine, contained ethyl chloride and dichloroethane[159-161].

Governale, Huguet, and Neher[162] have also chlorinated alkanes to alkyl chlorides photochemically.

Brow and Panis[163] chlorinated propane photochemically at 50° in a liquid medium consisting of polychloropropanes. The product contained 79.7% of chlorine, and was passed together with more chlorine into a salt bath containing equimolar amounts of potassium and zinc chlorides heated to 428°; the reaction product contained carbon tetrachloride, tetrachloroethylene, hexachloropropane, and hexachlorobenzene.

The productivity per unit volume of reaction mixture is considerably greater in the photochemical chlorination of ethane and propane than in the thermal chlorination; this fact merits particular attention.

Pritchard, Pyke, and Trotman-Dickenson[164] studied the rates of the light-induced reaction of chlorine with methane, ethane, propane, isobutane, neopentane, cyclopentane, methyl chloride, and ethyl chloride. They found that methyl chloride is more easily chlorinated than methane, but ethyl chloride less easily than ethane. The rate of reaction of chlorine atoms with hydrogen-containing compounds is very sensitive to the presence of traces of impurities, the surface condition of the reaction vessel, and, in photochemical processes, the intensity of the absorbed light. Tamura[165] found the upper limit of the energy of activation of the reaction

$$Cl\cdot + CH_4 \rightarrow CH_3 + HCl$$

to be 6 kcal/mole.

La Mare and Vaughan[166] also showed that ethyl chloride is less easily chlorinated than ethane, and that at elevated temperatures (above 280°) large amounts of ethylene and 1,1-dichloroethane are formed. Schumacher and Wolf[167] found the energy of activation for the reaction of Cl_2 with chloroform to be less than 4.3 kcal/mole.

Topchiev and Krentsel'[168] chlorinated *n*-butane photochemically in the annulus between two concentric glass tubes 44 and 40 mm in diameter and 600 mm long. The experimental results show that, in contrast to the thermal chlorination of butane, increasing the excess of hydrocarbon in the reaction mixture, even to a 10-fold proportion, does not lead to the formation of monochlorobutanes alone; under all conditions products boiling higher than the monochlorobutanes were obtained in considerable amounts; analysis showed that these were all dichlorobutanes. The formation of dichlorobutanes is apparently due to the action of light, which causes more extensive chlorination of the hydrocarbon. The monochlorobutane mixture has the same composition as the product obtained in the thermal chlorination of butane. In photochemical and catalytic chlorination, the reduction of the reaction temperature (because of the catalyst or photochemical effect) always leads to a much greater production of dichloro derivatives.

According to published data[169] the photochemical chlorination of isobutane takes place to a considerable extent on the surface of the reaction vessel.

TABLE 5.

Chlorination products	Initiator					
	benzoyl peroxide		azodiisobutyronitrile		dimethyl percorbonate	
	g	wt.%	g	wt.%	g	wt.%
Ethyl chloride	68.73	34.8	51.27	26.3	36.12	24.9
Polychloroethanes	128.51	65.2	143.48	73.7	109.00	75.1
Totals	197.24	100	194.75	100	145.12	100

Cantzler, Krekeler, and Leutner[170] prepared monochloro derivatives by the liquid-phase chlorination of hydrocarbons which are gaseous or highly volatile under normal conditions, using catalysts or irradiation to accelerate the reaction. Vajta, Toperczer, and Lengyel[171] used X-rays to accelerate the chlorination of paraffins.

Highly chlorinated products are obtained by chlorinating the higher paraffins in the liquid phase while irradiating with a mercury lamp; for example, with hydrocarbons having 10–16 carbon atoms, commencing the chlorination at 75° and gradually raising the temperature to 160° gives products containing 60% of chlorine[172]. In this connection it is interesting to note a new method now being developed for the extensive chlorination of high-molecular-weight hydrocarbons, in which chlorination is effected in liquid chlorine as solvent[173,174].

V. INITIATED CHLORINATION

At the present time great interest is being shown in initiated chlorination. The introduction into the reaction zone of substances which can form radicals in considerable quantities facilitates the decomposition of chlorine molecules into atoms and enables the chlorination to be effected at lower temperatures.

The use of organic peroxides for the chlorination of paraffins is suggested in the American patent literature[106]. The chlorination of hexane and other saturated hydrocarbons is accelerated at temperatures below 200° in the presence of organic peroxides such as ascaridole (Δ^2-*p*--menthene-1,4-dioxide).

Vaughan and Rust[10] described the chlorination of lower paraffins using lead tetraethyl as initiator. It has long been known that lead tetraethyl may be used as a source of ethyl radicals, which are easily formed by thermal decomposition above 200°. For example, ethane and chlorine react in the presence of lead tetraethyl at 132°, i.e. at a temperature 150°–250° lower than that of the purely thermal chlorination. It is remarkable that propane is chlorinated even at 0° in the presence of lead tetraethyl. In both cases about 95% of the chlorine reacts, and the chlorination of *n*-pentane in the liquid phase with $Pb(C_2H_5)_4$ as initiator takes place to the same extent.

Kharasch and his coworkers[107] studied the chlorination of paraffins with sulphuryl chloride in the presence of very small quantities (0.05%) of various organic peroxides; the most effective were benzoyl and lauroyl peroxides. In his review, Hass[7] considers in detail the combined action of SO_2 and Cl_2 on paraffins. He does not think it surprising that sulphur dioxide "initiates" the substitution of hydrogen by chlorine; in this he is in complete agreement with Deanesly's work[110] on the "induced" chlorination of paraffins in the presence of olefines, which is in accord with the theory of chain reactions.

Franck[176], Terenin[177], and Kondrat'ev[178] detected and discussed theoretically the decomposition of molecules into atoms or free radicals by the action of light quanta of sufficiently short wave length. Thus acetone decomposes to form $CH_3^{\cdot}$ with light of wave length 2540 Å. This method of initiating a chain reaction is notable in that definite quantities of primary radicals can be produced.

The present authors[179,180] have studied the low-temperature chlorination of ethane in the presence of initiators (benzoyl peroxides, azodiisobutyronitrile, and dimethyl percarbonate), using an ethane fraction containing 0.2 vol.% of ethylene and 1% of oxygen, with carbon tetrachloride as solvent. The experiments were carried out on a continuous basis in a glass column fitted with a jacket, a glass atomiser, a thermometer, and a reflux condenser. The column contained about 0.7 litre of CCl_4 with 1 mole % of initiator. Table 5 gives the results of a series of chlorinations with a chlorine to ethane ratio of 1 : 2.5 and a methane feed-rate of 45 h^{-1} [volumes per hour? Original reference not available for checking (Ed. of Translation)].

25–35% of ethyl chloride and 65–75% of polychloroethanes are formed. The polychloro fraction contains ~11% of trichloroethane, 27% of tetrachloroethane, and 12% of pentachloroethane. With chlorine to ethane ratios of 1 : 2.5 and 1 : 1.7, the ethane conversions are ~30% and ~60% respectively. It was shown that complete utilisation of chlorine is attained at 60°–70°, with a contact time of 36 sec, a benzoyl peroxide concentration of ~0.25 mole %, and $Cl_2 : C_2H_6 = 1 : 1$. The efficiency of the initiators falls off with time in the order benzoyl peroxide, azodiisobutyronitrile, dimethyl percarbonate.

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THE HYDRIDES OF THE RARE-EARTH METALS

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INTRODUCTION

Whilst developing methods of physicochemical analysis, Kurnakov has paid particular attention to one of the fundamental questions of inorganic chemistry — the definition of the concept of a chemical compound and its relation to the concept of a solution[1,2].

The concept of "berthollide" phases, with no singular points, was put forward by Kurnakov in his study of metallic alloys and has since proved applicable to other classes of inorganic compound. In particular, Kurnakov has pointed out[1] that hydrides of the transition metals form interesting examples of phases of variable composition. Kurnakov considered that berthollide phases are based on compounds present in a dissociated state. Deeper study of the properties of metallic berthollide compounds[3,4] led to the theory that the metals were exhibiting variable valency, the dissociation being regarded as a mobile equilibrium between different valency states of one of the components. In the study of metallic phases, however, such a conclusion can only be reached from a study of the composition–property diagrams constructed both experimentally and on the basis of the law of mass action. It is impossible to prove the existence of different compounds within a range of metallic berthollide phases either by preparative methods or by X-ray structural analysis.

Work in recent years has shown that the chemistry of the hydrides reveals greater possibilities for understanding the nature of phases of variable composition than the chemistry of metals, since in the study of the former the construction of the composition–property diagrams can be supplemented by synthesis of the hydrides and their derivatives by reaction between the metal salts and various reducing agents in non-aqueous media. The unique position of hydrogen relative to the other elements leads to great variety in its compounds. The fact that hydrogen reacts with almost all the elements in the Periodic Table to form many types of chemical bond makes it possible to clarify the chemical character of other elements from the properties of their compounds with hydrogen.

In recent years considerable attention has been paid to the hydrides of the rare-earth metals, because of their chemical nature and the possibility of their practical application in metallurgy, vacuum technology, inorganic synthesis, etc.

In spite of the fact that rare-earth metal hydrides have been known for a considerable time, they had not until recently been studied in sufficient detail to enable any conclusions to be drawn regarding the nature of the chemical bonding of the hydrogen in these compounds.

An increasing amount of work devoted to their preparation, composition, and properties has appeared in the past few years. The aim of the present article is to summarise the published material in this field.

I. Reaction of the Rare-Earth Metals with Hydrogen

A general method for the preparation of the rare-earth metal hydrides is by the direct reaction between the metal and hydrogen. Sometimes the reaction proceeds fairly vigorously even at room temperature, but in other cases direct hydrogenation by molecular hydrogen at low temperatures is fairly slow. When this is so, for example with cerium, the metal is given a preliminary thermal treatment by heating in vacuo[5]. Several workers have related the resultant activation to the formation of microscopic cracks which facilitate the penetration of hydrogen into the metal[6]. It has also been suggested that the activation is related to the dissolution, at the high temperature, of cerium oxides blocking the metal surface. Dialer[7,8] has shown that the

activation of cerium by thermal treatment is related to the conversion of the β-form of the metal, which is inert towards hydrogen, to the active γ-form.

In recent years, hydrides of the transition metals have also been prepared by exchange reactions in aqueous and non-aqueous media, such as the well-known method for the preparation of copper hydride by the reaction between copper salts and hypophosphites in aqueous solution [9,10]. This method, however, is not generally applicable to the rare-earth elements, in view of the marked chemical reactivity of their hydrides.

The hydrides of the elements of the iron family and the vanadium and tungsten sub-groups can be obtained by the reaction between their halides and phenyl magnesium bromide in an atmosphere of hydrogen [11-16]. The hydrides of zinc and cadmium are obtained by the reaction with lithium aluminium hydride in ethereal solution [17]. Analogous methods have been tried for the rare-earth metals. The reaction between ethereal solutions of cerium bromide and lithium aluminium hydride gives not the simple hydride but a yellow precipitate of the double hydride of cerium and aluminium $Ce(AlH_4)_3$. [18-20]

The synthesis of double boro- and aluminohydrides of many of the transition metals [21-22] is important in confirming the existence of their simple hydrides. The generally-accepted principle that simple compounds can be stabilised by complex formation, suggests, for example, that the existence of the compound $M(BH_4)_n$ provides evidence that the existence and synthesis of the simple compound MH should be possible.

1) Lanthanum and Hydrogen

According to Winkler [23], Matignon [24], Muthmann et al. [25-27], Sieverts [28], and others, "lanthanum mischmetall", i.e. an alloy of lanthanum with smaller quantities of other rare-earth metals, reacts with hydrogen when finely divided even at room temperature. As the hydrogen is absorbed, voluminous grey-black platelets separate from the metal particles, since the hydrogenation of the lanthanum is accompanied by a 13% increase in volume.

The composition of lanthanum hydride, according to Winkler [23], corresponds to the formula LaH_2 (1.43 wt. % H, 66.7 at. % H), and according to Muthmann and Kraft [27], to the formula LaH_3 (1.95 wt. % H, 69 at. % H). Recent data [29] indicate that saturation of lanthanum with hydrogen at room temperature gives a product of composition LaH_3. The preparation of the deuteride LaD_3, with properties similar to those of lanthanum hydride, has been reported by Viallard [29].

According to Sieverts [30], the density of the lanthanum hydride $LaH_{2.76}$ is 5.83 g/cm^3, while that of LaH_2, calculated from X-ray diffraction data, has been found to be 5.14 g/cm^3. [31]

The heat of formation of a hydride with composition $LaH_{2.76}$ is 40.09 kcal/mole H_2 [28], i.e. it is of approximately the same order of magnitude, per unit valency, as the heat of formation of the alkali and alkaline-earth metal hydrides. According to Mulford and Holley [32], the heat of formation of lanthanum dihydride is slightly higher, and equal to 49.7 kcal/mole H_2.

Sieverts [5,30,33] found that the hydrogen content of lanthanum hydride specimens depends on the pressure of hydrogen above the metal, and that for the same hydrogen content, the pressure increases with increase in temperature. He therefore regards lanthanum hydride not as a definite compound, but as a solid solution of hydrogen in lanthanum. More accurate measurement of the dissociation pressure of lanthanum hydride has shown, however, that the pressure is constant up to the composition LaH_2 [32]. When the lanthanum absorbs greater quantities of hydrogen, there is a sharp increase in the dissociation pressure. The authors [32] conclude that two solid phases exist in the range $La-LaH_2$, while the range LaH_2-LaH_3 consists of a single phase, probably a solid solution of hydrogen in lanthanum dihydride.

In recent years lanthanum hydride has been studied a great deal, particularly by X-ray diffraction methods. Rossi [34,35] found that a specimen containing 200 cm^3 H_2 per g of metal ($LaH_{2.5}$) has a cubic lattice with a = 5.63-5.64 Å. Work by Holley, Zachariasen and others (involving X-ray and neutron diffraction studies [31]) on the dependence of the equilibrium pressure on the temperature and concentration [32] showed, together with microstructural examination, that below a hydrogen content corresponding to the composition LaH_2 (1.43 wt. % H, 160 cm^3 H_2 per g), the alloys consist of two phases — the metal and the hydride. The hydride LaH_2 has a face-centred cubic lattice of the CaF_2 type with a = 5.667 Å, and is able to dissolve more hydrogen: at the approximate composition $LaH_{2.39}$ (70.6 at. % H) the lattice parameter decreases to 5.63 Å. The extra hydrogen atoms in the hydrides containing more hydrogen than corresponds to the formula LaH_2 are randomly distributed in the octahedral holes of the face-centred cubic lattice. It has been suggested that a hydrogen pressure of more than one atmosphere is necessary to obtain a product with the composition LaH_3.

Earlier work by Stalinsky [36] on specimens of composition LaH_2-LaH_3 showed a change in the parameter of the face-centred cubic lattice within the range 5.66 Å to 5.60 Å. Measurement of the density of specimens of composition $LaH_{0.1}-LaH_{2.97}$ by the same author confirmed the contraction of the crystal lattice in the range between LaH_2 and LaH_3. Analogous data on the existence of two phases in the range $LaH-LaH_2$ were obtained by Dreifus-Allain [37-38], who showed that in the gradual hydrogenation metal and hydride exist together up to hydrogen pressures of 2.9 mm Hg. Above this pressure the lattice changes sharply and only the hydride remains. Similar effects were observed in the combination of lanthanum and deuterium [39].

The La-H phase diagram has recently been studied using a high-temperature powder camera [40]. It was found that even when the hydrogen content is extremely low, the hexagonal modification of lanthanum changes above 240° to the high-temperature modification with a = 5.29 Å and is not re-formed, even when cooled in liquid nitrogen.

In 1957 Stalinsky studied the magnetic properties of lanthanum hydrides [41], and found that the magnetic susceptibility decreases with increase in the hydrogen content. In the range $La-LaH_2$, the susceptibility decreases with increase in temperature in the range 120°-290°K, whereas that of specimens of composition LaH_2-LaH_3 remains constant.

Measurement of the electrical conductivity in the homogeneous region of the La-H system (LaH_2-LaH_3) has shown that the hydride is a semiconductor [42].

2) Cerium and Hydrogen

Cerium is the most readily available lanthanide, and its hydride has been studied in most detail. The chemical and physical properties of the rare-earth metal hydrides are typified by those of the cerium compound.

As early as 1891 Winkler [23] showed that the cerium which is obtained as a spontaneously inflammable dark brown powder by the reduction of cerium oxide with magnesium

contains a considerable quantity of hydrogen; he even suggested that a definite compound CeH_2 (1.41 wt. % H) was formed. He also suggested that the reaction of cerium with hydrogen requires the high temperature reached in the reaction with magnesium and also that the cerium must be present in the freshly-reduced state. Matignon[24], however, obtained cerium hydride by direct hydrogenation of the compact metal.

The hydrogenation of cerium was subsequently studied by Muthmann and Kraft[27], Muthmann and Bauer[25], Kellenberger and Kraft[43], Whitehouse[44], Lipsky[45], Dafert and Miklaus[46], and Zhukov[47]. In the nineteen-twenties the hydrides of the transition metals and the hydrogenation of cerium in particular were investigated by Sieverts et al.[5,28,33,48], but the absence of data on the hydrides of cerium and the other rare-earth metals in the literature of the thirties and forties shows that interest in these compounds had then weakened. In the fifties, however, the study of the rare-earth hydrides, and of cerium hydrides in particular, developed simultaneously in a number of countries, and new and interesting results appeared.

The kinetics of cerium hydrogenation. According to Muthmann and Kraft[27], metallic cerium absorbs hydrogen at 250°–270° to form a reddish-brown mass containing 1.74–3.19 wt. % H (average 2.4 wt. % H). Zhukov[47] established that cerium starts to react with hydrogen at 300° and that the reaction is extremely rapid at 400°; in 1923 Sieverts[5] concluded that cerium was activated by heating or fusion for a short time in vacuo, after which the metal starts to absorb hydrogen even at room temperature.

In 1948 Dialer[49] studied the relationship between the rate of absorption of hydrogen by pure cerium at 20° and the temperature of the preliminary heat treatment of the metal. He found that increase in the temperature of the pre-treatment increases the rate of absorption of hydrogen up to an optimum value corresponding to the thermal treatment at 650°. The decrease in the activity of specimens after pre-treatment at 845° was explained by the author as due to fusion of the cerium, leading to a decrease in the number of active hydrogenation centres. In subsequent work Dialer and Rothe[7] established that β- and γ-cerium at room temperature[50,51] behave differently towards hydrogen: γ-Ce absorbs hydrogen without preliminary thermal treatment, while β-Ce does not react with hydrogen. γ-Ce can be converted to β-Ce by heating to 70°.

Mikheeva and Kost[20,52] studied the rate of reaction of cerium with hydrogen at different temperatures and showed that compact metallic cerium will absorb hydrogen even at room temperature without preliminary thermal treatment, if the hydrogen is thoroughly purified. The curve showing the relationship between the hydrogenation time (to saturation) and the temperature (Fig. 1) shows three branches — — two descending and one ascending.

Comparison of these data with the composition curve (Fig. 2, curve *a*) shows that the descending branches of the curve in Fig. 1 correspond to the formation of cerium trihydride and dihydride, while the decrease in the rate of hydrogenation with increase in temperature corresponds to the formation of hydrides of variable composition in the range CeH_2–CeH_3.

The composition of cerium hydrides. Sieverts and Roell[33] showed that the quantity of hydrogen absorbed by cerium decreases with increase in the temperature, and that the smooth temperature–composition curve for the hydride shows a sharp inflection at 1100°–1200°,

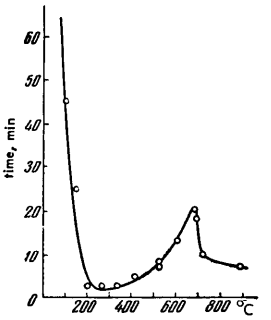


Fig. 1. Relationship between the time of hydrogenation of cerium and temperature[20].

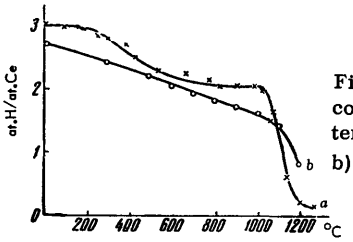


Fig. 2. Relationship between the composition of cerium hydrides and temperature: a) Mikheeva and Kost[20]; b) Sieverts and Roell[33].

indicating that cerium hydride decomposes appreciably above 1100° (Fig. 2, curve *b*).

Since practically no reaction between cerium and hydrogen is observed below 0°,[25] most authors achieve maximum saturation of the hydrides by rapid cooling to room temperature.

Muthmann[27] obtained a high degree of saturation of cerium by hydrogen, but the reproducibility of the separate experiments was poor (Table 1). Sieverts[5,28], using the thermal treatment, obtained more stable results, but the hydrogen concentration of his specimens was much lower, and did not reach the composition CeH_3. A recent paper on the rare-earth metal hydrides[31] still reports that it is impossible to obtain cerium "trihydride" without using increased pressure of hydrogen.

Using improved methods for purifying the starting materials Dialer[49] in 1948 prepared cerium hydride of stoichiometric composition CeH_3 from mischmetall, the hydrogen content being referred to pure cerium; in 1955 he obtained cerium trihydride by hydrogenating pure cerium at room temperature[7,8]. This was also achieved by Mikheeva and Kost[20,52] showed that the curve relating the composition of cerium hydrides and temperature (Fig. 2, curve *a*) has two plateaux corresponding to the compounds CeH_3 and CeH_2 (contrary to Sieverts' data[33]). This shows that the two hydrides exist over definite temperature ranges[20]. The trihydride is obtained by the reaction between cerium and hydrogen at room temperature, and the dihydride can be obtained by heating the trihydride for half an hour at 400°. The composition of the cerium hydride formed at room temperature is independent of the hydrogen pressure, and the limiting hydrogen content corresponds to the formula $CeH_{3.15}$[20].

The dissociation pressure of cerium hydrides. In their first experiments, Muthmann and

Bauer[25] found that the dissociation pressure of cerium hydride for a given temperature was not reproducible, being different after reheating. The authors concluded that the dissociation of cerium hydride was irreversible in the temperature range up to 740°. They ascribed this phenomenon to an irreversible change in the molecular structure of the hydride.

In a study of the dissociation isotherms at 480° and 450°, Zhukov[47] found that the pressure remained constant (~ 1 mm Hg) up to 160 cm^3 H_2 per g Ce, i.e. up to a composition corresponding to cerium dihydride. Further increase in the hydrogen content leads to a sharp increase in the pressure. Zhukov took this to indicate the existence of the compound CeH_2.

Sieverts and Müller-Goldegg[5] studied the isotherms over a wider temperature range. Detailed study of the 800° isotherm showed that they all consist of three clearly-defined branches. The first ascending branch shows a very slight increase in the pressure from 0 to several mm Hg. This is followed by a horizontal branch almost coinciding with the x-axis, and this in turn is followed by a third branch which rises steeply. Analogous curves with good reproducibility were obtained by Dialer[49].

Owing to inaccuracy in the measurements at low pressures, the start of the third branch was displaced with decrease in the temperature, which contradicted Zhukov's conclusion that cerium dihydride is formed. More detailed study with accurate measurement of the low pressures[32], however, subsequently confirmed Zhukov's conclusion that cerium dihydride exists up to 800° (Fig. 3).

Fig. 3 shows that the dissociation pressure at 500°–800° remains constant up to the approximate composition CeH_2, which indicates that two phases exist in this range: the metal, saturated with hydrogen, and cerium dihydride. When one of the phases disappears (in this case the metal) a very slight increase in the hydrogen content leads to a sharp increase in the pressure.

The isotherms for lower temperatures (Fig. 4) show that the CeH_3–CeH_2 system most probably consists of a solid solution of hydrogen in cerium dihydride[32].

The structure of cerium hydrides. Conclusions based on the dissociation pressure of cerium hydrides are confirmed by recent X-ray diffraction studies.

Until recently the only such work was by Rossi[35], who reported that cerium hydride has a face-centred cubic lattice with lattice parameter a = 5.61 Å. Removal of hydrogen by evacuation at 530° leads to the appearance of a second phase with a slightly smaller lattice period.

In 1955, Zachariasen et al.[31] described the crystal structure of rare-earth metal hydrides, including cerium hydrides of composition CeH–$CeH_{2.7}$, and found that specimens containing less than two hydrogen atoms per metal atom consist of a mixture of metal and hydride with lattice parameter a = 5.581 ± 0.001 Å. Close to the composition CeH_2, the lattice of the metal disappears leaving only that of the hydride CeH_2, which is of the CaF_2 type with the above parameter. Further increase in the hydrogen content causes a gradual decrease in the lattice parameter, which reaches the value a = 5.540 ± 0.003 Å for $CeH_{2.47}$. Specimens of higher hydrogen content were not studied.

Kost and Gol'der[53] obtained analogous data showing the presence of two phases in the range $CeH_{0.2}$–CeH_2, with lattice parameters a' = 5.13 Å and a'' = 5.55 Å. They also studied specimens of higher hydrogen content and confirmed

TABLE 1. Composition of cerium hydride showing maximum saturation with hydrogen.

At. H / At. Ce	Deviation in separate experiments	Method of analysis	References
3.4	±0.9	from increase in weight	27
3.03	±0.2	»	46
2.75	±0.05	»	5
2.60	±0.1	»	28
3.00	±0.01	by ignition and volume measurement	49
3.00	±0.1	by volume measurement	20,52

that the lattice parameter decreases when cerium dihydride absorbs more hydrogen. Specimens of composition $CeH_{2.73}$ consist of a homogeneous phase with parameter a = 5.53 Å. As the composition approaches CeH_3, the lines in the powder diffraction pattern become broader, which makes exact calculation of the lattice parameter difficult.

Auphassorho[54–56] detected two new phases. As cerium dihydride absorbs hydrogen and approaches the composition CeH_2, a new phase (γ) with parameter 5.645 ± 0.003 Å was observed in addition to the β-phase with parameter 5.581 Å. With further absorption of hydrogen, the intensity of the lines of the β-phase decreases, with a simultaneous decrease in the parameter of the γ-phase. When the lines corresponding to the β-phase have disappeared completely, at a hydrogen pressure of 4 mm Hg, a single lattice with parameter 5.634 ± 0.0004 Å remains. Increase in the hydrogen pressure to 38 mm Hg leads to a decrease in the parameter to 5.612 ± 0.003 Å. The author relates the appearance of this new phase to a difference in the hydrogen distribution

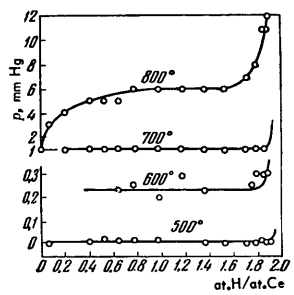


Fig. 3. Dissociation-pressure isotherms for cerium hydrides in the range Ce – CeH_2.[32]

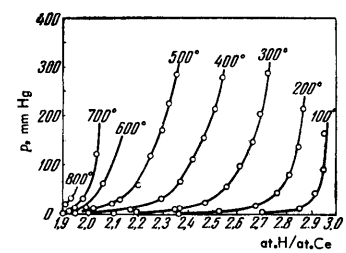


Fig. 4. Dissociation-pressure isotherms for cerium hydrides in the range CeH_2–CeH_3.[32]

in the cerium lattice, assuming that in the β-phase all the tetrahedral holes in the cubic face-centred lattice are occupied, while in the γ-phase the hydrogen atoms are situated in octahedral holes. In his most recent work[56], the formation of another phase in the Ce–H system is reported. Specimens containing this phase were obtained by prolonged heating (500 h at 300°) of cerium dihydride with lattice parameter a = 5.590 Å, which yielded a hydride of composition $CeH_{0.7\pm0.2}$ with lattice parameter a = 5.04 ± 0.01 Å. The author attributed the appearance of this phase to redistribution of the hydrogen atoms in the octahedral holes. In view of the lattice contraction which takes place, he suggested that the new hydride is analogous in chemical character to the alkali-metal hydrides.

The physical properties of cerium hydrides. The earliest pyknometric data obtained by Sieverts and Gotta[28] using petroleum ether as flotation medium gave the average density of material of composition $CeH_{2.69}$ as 5.55 (±3%) at 25°, compared with the value 6.734 for the original cerium. The absorption of hydrogen thus leads to a decrease in the density by 17.5%, i.e. an increase in specific volume of 21.6%.

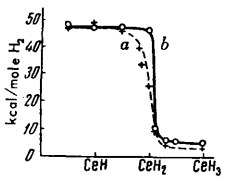


Fig. 5. Heat of formation of cerium hydrides vs. composition[8]:
a) calculated; b) experimental.

Kost and Gol'der[53] measured the density of hydride specimens in the concentration range $CeH_{0.2}$–CeH_3 by the "argon" method. The density–composition curve shows a decrease in the density with increase in the hydrogen content, followed by a minimum approximately at the composition CeH_2 (d_{20} = = 5.4 g/cm³) and a slight increase in the density with further approach to the trihydride composition (d_{20} = 5.5 g/cm³).

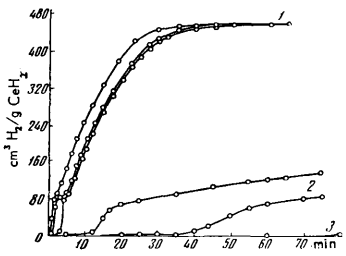


Fig. 6. Hydrolysis of cerium hydride[60]; 1) CeH_3 at 20°; 2) CeH_3 at 0°; 3) CeH_2 at 20°.

The heat of formation of cerium hydride, determined by dissolution in hydrochloric acid[28], amounts to 42.26 kcal per mole of combined hydrogen. A more detailed study of the heat of formation of cerium hydrides of different composition was made by Dialer[7,49] who constructed log p vs. $1/T$ curves from data on the dissociation pressure of the hydrides. The curve for the heat of formation of various hydrides (Fig. 5, curve a) shows good agreement with the data from the direct calorimetric determination involving dissolution of the cerium hydrides in acid (Fig. 5, curve b). Both curves show a sharp drop close to the composition CeH_2, which indicates that the attachment of the third hydrogen atom to the cerium dihydride is accompanied by a much smaller heat of reaction than the addition of the first two hydrogen atoms.

The change in the electrical conductivity of cerium powders during hydrogenation is of particular interest. Daou[57] was the first to overcome the considerable experimental difficulties involved and measure these changes. He found that the resistance increases by a factor of several hundreds during the hydrogenation of cerium up to a cerium : hydrogen ratio of 1 : 1, after which the resistance starts to decrease. The hydrogenation was found to be reversible. In 1958 Daou improved his technique and measured the electrical resistance of cerium during hydrogenation up to a composition $CeH_{2.4}$ [58]. Under these conditions the resistance of the cerium decreases linearly by 30% as the composition CeH_2 is approached ($CeH_{1.8}$), after which it rises steeply. The author attributed this to the increased metallic character of the hydride CeH_2 resulting from movement of the 4f electrons to the s level and back, i.e. he put forward an explanation similar to that of Zachariasen et al.[31]. In the same work the author detected an anomalous change in the resistance during thermal treatment in the composition range close to CeH.

The magnetic properties of the Ce–H system were studied by Albany[59], who detected anomalous ferromagnetism in the range $CeH_{1.9}$–CeH_2. The author himself suggested, however, that this effect was due to iron impurities.

The chemical properties of cerium hydrides. Cerium hydride with highest hydrogen content is a highly reactive brittle flaky grey-blue material. The freshly-prepared hydride reacts with nitrogen even at room temperature[45] and when heated to 800°–900° is completely converted to the nitride. It is spontaneously inflammable in air[23,25] and burns to form a mixture of oxide and nitride. This makes it difficult to work with, but a short treatment with dry carbon dioxide brings about surface passivation, which makes it possible to handle specimens for short periods in air[60].

Cerium hydride dissolves readily in dilute acids with evolution of hydrogen:

$$CeH_3 + 3HCl = CeCl_3 + 3H_2.$$

This reaction is used for the quantitative estimation of the hydrogen in these hydrides.

Cerium trihydride reacts fairly vigorously with water even at 0°,[60] liberating hydrogen and forming white cerium hydroxide:

$$CeH_3 + 3H_2O = Ce(OH)_3 + 3H_2.$$

Cerium dihydride reacts with water much more slowly than the trihydride (Fig. 6)

Cerium hydride precipitates many heavy metals from solutions of their salts. It forms explosive mixtures with nitrates and perchlorates. No vigorous reaction is observed with gaseous chlorine at room temperature, but an explosion takes place on heating. The reaction with hydrogen bromide at 500°–600° is vigorous and can be used to prepare anhydrous cerium bromide[60].

Cerium di- and trihydride differ considerably in their thermal stability. The trihydride begins to decompose at ~200°, whereas the dihydride is stable up to 800°–900° [20] (Fig. 7). Vigorous decomposition begins only after fusion at 1080°, and even at 1200° the hydrogen is not removed completely [20].

Double hydrides of cerium and aluminium. Until recently nothing was known of double hydrides of the rare-earth metals [21, 22], but an aluminohydride of trivalent cerium has now been synthesised [18–21]. The double hydride $Ce(AlH_4)_3$ is obtained by the reaction between cerium bromide and an ethereal solution of lithium aluminium hydride at -79°. [20] It consists of an extremely reactive yellow powder, which decomposes gradually to the elements when heated to -40°.

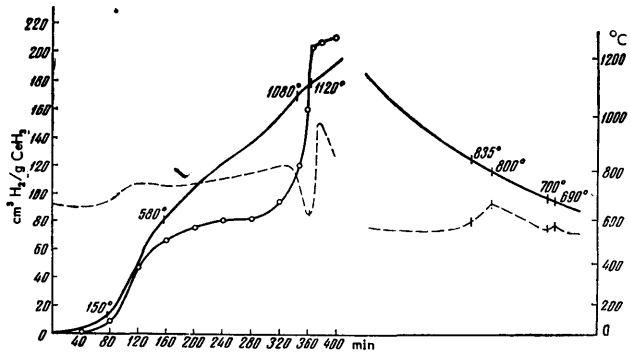


Fig. 7. Thermogram for the CeH_3 decomposition [20].

3) Praseodymium and Hydrogen

According to Muthmann and Beck [61], praseodymium does not react with hydrogen at room temperature and absorbs the gas actively only at 300°–400° with the formation of a brittle green product.

According to Sieverts and Roell [60], hydrogenation yields a product with composition close to PrH_2, but the authors suggest that the substance is not a definite compound but a solid solution, since the compounds PrH_2 and PrH_3 contain 1.40% and 2.08% of hydrogen respectively, while the material obtained on hydrogenation contains 1.68% H. The hydrogen pressure–hydrogen content curves are analogous to those for the cerium–hydrogen system [28, 32].

The density of the material of composition $PrH_{2.84}$ is 5.56 g/cm³, i.e. 14.6% less than that of the compact metal; the heat of formation of the same specimens is 39.52 kcal per mole H_2 [41]. In a recent paper [32], the heat of formation of PrH_2 was calculated from data for the dissociation pressure of the hydride and found to be 47.8 kcal/mole.

Rossi [35] has investigated the structure of praseodymium hydride and found that the β-modification has a hexagonal close-packed lattice with a = 3.65 Å and c/a = 1.61. In 1955 Mulford and Holley studied the dissociation pressure and crystal structure of praseodymium hydride and concluded that two phases, with cubic face-centred lattice, exist in the range $Pr–PrH_2$, after which a solid solution of hydrogen in the dihydride is formed (a = 5.517). The density of the dihydride is 5.65 g/cm³. [31]

4) Neodymium and Hydrogen

The properties of neodymium hydride are analogous to those of praseodymium hydride [24,31,32,61,62]. On hydrogenation metallic neodymium is converted to a dark-coloured powder with a hydrogen content corresponding approximately to the formula NdH_2. The dissociation-pressure isotherms and X-ray diffraction data [31,32] indicate the existence of neodymium dihydride with lattice parameter a = 5.470 Å and density 5.94 g/cm³. The heat of formation calculated from the dissociation-pressure data is 44.8 kcal [32].

5) Samarium and Hydrogen

Metallic samarium reacts with hydrogen at high temperatures forming a product of composition SmH_2, which dissociates readily on further heating [24]. Like the hydrides of other rare-earth metals, samarium hydride has a face-centred cubic lattice of the CaF_2 type with $a = 5.376 \pm 3$ Å and density 6.52 g/cm³. [23]

According to recent work [63], maximum saturation with hydrogen corresponds to the hydride SmH_3. There are reports [64] that samarium trihydride is isostructural with plutonium trihydride PuH_3, i.e. it has a hexagonal lattice [65,66].

6) Europium and Hydrogen

Europium hydride and deuteride have been studied by Korst and Warf [63,67]. In contrast to the behaviour of other rare-earth elements, the absorption of hydrogen by europium up to the composition $EuH_{1.96}$ is accompanied by a considerable lattice contraction and a resultant increase in the density by 12.5% compared with the original metal.

The resemblance of europium hydride and deuteride to the salt-like hydrides is confirmed by their structure, which is analogous to that of strontium hydride SrH_2. Europium deuteride has lattice parameters a = 6.21 Å, b = 3.77 Å, and c = 7.16 Å (±0.02 Å) [67].

7) Gadolinium and Hydrogen

The conditions for the reaction of hydrogen and deuterium with gadolinium were first studied by Viallard [68,69] who found that hydrogen and deuterium react with gadolinium above 150° to form Gd_2H_3 or Gd_2D_3 respectively, and that Gd_2H_3 can be converted to GdH_2 by cooling in a current of hydrogen.

The compounds GdH_2 and GdD_2 are stable at room temperature, but dissociate when heated above 250°, forming the original compounds Gd_2H_3 and Gd_2D_3 [69]. The actual composition of these compounds, however, deviates slightly from these formulae.

The dissociation-pressure isotherms for gadolinium hydride have been constructed by Sturdy and Mulford [70]. In contrast to the systems formed by hydrogen with lanthanum, cerium, neodymium, and praseodymium, the gadolinium–hydrogen system gives isotherms with two horizontal plateaux: one in the range $Gd–GdH_2$ and one in the range $GdH_2–GdH_3$. This led the authors to suggest the existence of two hydrides GdH_2 and GdH_3, which has been confirmed by X-ray analysis [31]. The first plateau corresponds to the coexistence of metal and dihydride, with face-centred cubic lattice (a = 5.303 ± 0.001 Å), as in the cerium–hydrogen system.

The second horizontal plateau corresponds to the two-phase region GdH_2-GdH_3. Gadolinium trihydride is isomorphous with PuH_3 and has a hexagonal lattice with parameters $a = 3.73 \pm 0.01$ Å and $c = 6.71 \pm 0.02$ Å. The density of gadolinium dihydride calculated from the X-ray structure date is 7.08 g/cm³, while that of the trihydride is 6.57 g/cm³. [70]

The authors [64,70] have also given the phase diagram for the Gd–H system and have calculated the heat of formation of gadolinium dihydride, 46.9 kcal/mole.

8) Ytterbium and Hydrogen

According to Korst and Warf [63,67], the saturation of ytterbium with hydrogen to the composition YbH_2 leads to an increase in the density by 13.5%, as in the case of europium. The structure of ytterbium deuteride is analogous to that of SrH_2 and is orthorhombic with parameters $a = 5.871$ Å, $b = 3.561$ Å, and $c = 6.763$ Å. [60]

II. SOME PECULIAR FEATURES OF THE RARE-EARTH HYDRIDES

If we adopt the generally-accepted classification of inorganic hydrides [71–73] into the three classes — salt-like, covalent and metallic — we find that the hydrides of the rare-earth elements occupy a special position.

The salt-like hydrides are characterised by constant composition, electrovalent bonding, high heats of formation (30–40 kcal/mole H_2), and a density greater than that of the original metals (Proskurnin and Kazarnovskii [74]).

The volatile covalent hydrides formed by the elements in Groups IV–VII A also have constant composition and high heats of formation [75].

The class of metallic hydrides includes the hydrogen compounds of all metals in which the inner d and f levels are being filled. The products of the direct hydrogenation of these metals do not, in most cases, exhibit stoichiometric composition, and depend on the conditions under which the reactions are carried out. For most transition-metal hydrides, the composition is related to the hydrogen pressure by the equation [76,77]

$$m = k\sqrt{p_{H_2}}$$

or by the more exact formula derived by Fowler and Smithells [78]

$$\log m = 2.774 + 0.5 \log p - 0.25 \log T - \log d - \frac{\theta}{9.148\,T},$$

where m is the number of cm³ of hydrogen per 100 g of metal, p the pressure in mm Hg, T the absolute temperature, d the density of the hydride, and θ the heat of dissolution of hydrogen in the metal, in kcal/mole H_2.

The absorption of hydrogen by the transition metals is accompanied by a decrease in the density. Detailed study has shown, however, that within the transition metals there is a considerable difference in behaviour, and this is shown particularly clearly by the elements of the "extreme" groups. Thus, for example, the elements in Groups IB and IIB — copper, zinc and gold — are analogous to elements in the middle of the short periods (Be, B, Al) and under certain conditions form unstable volatile hydrides [78,80], so that these may be put in a separate class of the so-called polymeric hydrides [81]. On the other hand, the elements in Groups III–V differ essentially from the typical metallic hydrides and resemble the salt-like hydrides in their heats

TABLE 2. Heat of formation of certain hydrides.*

Hydride	Heat of formation, kcal/mole H_2	References	Hydride	Heat of formation, kcal/mole H_2	References
LiH	42.68	82	PuH_2	32.5	84
NaH	27.2		$TiH_{1.75}$	36.0	85
KH	30.32		$ZrH_{1.92}$	40.5	86
CaH_2	46.6	73	$CrH_{0.26}$	3.8	28
BaH_2	40.96		$PdH_{0.59}$	8.59	87
SrH_2	42.2		Mo*	−14.0	88
$CeH_{2.69}$	42.26	28	Co	−14.55	
$PrH_{2.84}$	39.52		Cu	−18.3	
$LaH_{2.46}$	40.09	83	Ni	−5.9	89
UH_3	20.6		Fe	−5.9	

* The heats of formation of the hydrides of molybdenum and succeeding metals were found from the slope of the $\log S - 1/T$ isobars, using the equation $\log S = \log S_0 + 0.5 \log P - \frac{\theta_3}{9.148} T$, where S_0 and P are constants.

of formation (Table 2), the quantities of hydrogen which they absorb, and the shape of their solubility isobars [77]. Nekrasov therefore puts them in a separate class of "intermediate" hydrides [81]. The hydrides of the rare-earth elements, which are closest to the alkaline-earth elements, should undoubtedly show these "intermediate" properties even more clearly.

The density changes also show the similarity to the salt-like hydrides. It has been mentioned that in contrast to the case of the ionic hydrides, the formation of the rare-earth metal hydrides is accompanied by a considerable decrease in the density (Table 3). Recent work has shown, however, that the nature of the change in the density is not a fundamental criterion in the classification of the hydrides. Thus by comparing atomic and ionic radii, Dialer [90] has shown that, for cerium in particular, the decrease in the density on hydrogenation may result from the small change in the volume of the atom on ionisation. Dialer's calculations for cerium are compared with data for the alkali metals in Table 4. The last column shows the change in volume per unit valency on going from the atomic to the ionic state.

TABLE 3. Density changes on hydride formation [90]

Hydride	Density of metal, g/cm³	Density of hydride, g/cm³	Change in density, %	Change in specific volume, %
LiH	0.534	0.816	+52.3	−34.2
NaH	0.97	1.4	+44	−31.1
KH	0.86	1.47	+71	~−41
RbH	1.52	~2	~+33	−24
CsH	1.87	2.7	+44	−30
CaH_2	1.55	1.7	+10	−9
BaH_2	3.5	4.21	+20	−17
$CeH_{2.69}$	6.73	5.55	−17.5	+21.6
$PrH_{2.84}$	6.51	5.56	−14.6	+16.9
$LaH_{2.76}$	6.69	5.83	−12.8	+15.4
$TiH_{1.62}$	4.52	3.91	−13.5	+15.5
ZrH_2	6.79	5.47	−19.4	+24.5
$VH_{0.56}$	5.68	5.30	− 6.7	+ 7.2
$CrH_{0.26}$	~7.0	6.77	− 3.7	+ 3.7
$PdH_{0.55}$	11.87	10.76	− 9.4	+10.3

Analysis of the data in Table 4 shows that in the case of alkali and alkaline-earth metal hydrides, the volume change per unit valency ($\Delta v/n$) is much greater than the volume of the negatively charged hydrogen ion. These compounds are therefore formed with a decrease in volume, whereas the volume made available by the ionisation of cerium (to Ce^{3+})

TABLE 4. Change in the volume of metal atoms on ionisation [90].

Metal	Atomic radius, Å	Ionic radius, Å	Atomic volume, Å³	Ionic volume, Å³	$\frac{\Delta v}{n}$
Na	1.86	0.98	26.9	3.9	23.0
Rb	2.36	1.49	55.1	13.9	41.2
Ca	2.21	1.06	45.2	5.0	20.1
Ce	1.69	1.18	20.2	6.9	4.4
H^-		1.27	—	8.58	—

TABLE 5. The atomic volume of hydrogen in hydrides [91].

Hydride	Mol. volume of hydride, found experimentally	Mol. volume of hydride, calculated for $T = 0$	Zero-temperature volume of metal	Volume of H in the hydride *
LiH	9.8	9.6	12.6	(3.3)
NaH	17.4	17.1	22.8	5.7
KH	27.3	26.8	43.4	5.1
RbH	33.3	32.6	53.1	6.0
CsH	39.1	38.3	65.9	5.3
CaH_2	24.8	24.6	25.5	5.9
BaH_2	33.1	32.8	38	6.9
$LaH_{2,76}$	24.3	24.1	20.4	5.0
$CeH_{2,69}$	25.7	25.4	20.4	5.7
$PrH_{2,84}$	25.8	25.5	21.2	5.3
$VH_{0,56}$	9.73		9.9	1.3
$CrH_{0,26}$	7.72		7.4	1.2
$PbH_{0,55}$	9.97		9.0	1.8

* These values were obtained by the author by subtracting half the zero-temperature volume of the metal from the zero-temperature molar volume of the hydride, as required by the preceding calculations in the same work.

is insufficient to accommodate the hydrogen anions, so that the formation of an ionic bond in hydrides of the transition metals, and the lanthanides in particular, may be accompanied by a decrease in the density.

On the other hand, Table 5 gives Biltz's data for the volume of hydrogen in various hydrides, calculated from the measured density and the ionic volume of the metal in question (Table 5, column 4) in its other compounds [91].

The last column in Table 5 shows that the hydrogen in the rare-earth metal hydrides occupies the same volume as in the ionic hydrides, whereas the volume of hydrogen in the metallic hydrides is much smaller.

Analogous results were obtained by Libowitz and Gibb [92] in their calculation of the ionic radius of hydrogen in various hydrides (Table 6). They started from the normal oxidation state of the metal (Table 6, column 4) assuming that the fraction of the electrons not taken up by the hydrogen take part in the formation of a residual metallic bond, which is responsible for the electrical conductivity of these compounds. The radius of the electronegative hydrogen (Table 7) decreases regularly with increase in the electronegativity of the cation and hence it may be assumed that the radius of the hydrogen anion in the intermediate hydrides will be less than 1.37 Å.

Table 6 shows that the average value is in fact 1.29 ± 0.05 Å. Since in the case of a covalent or metallic bond the hydrogen atom has a radius of 0.27–0.80 Å, the authors conclude that the hydrogen in the intermediate hydrides is ionic in character.

On the other hand, until recently the chief indication of the difference between the rare-earth metal hydrides and the salt-like hydrides has been the absence of stoichiometric relationships in the former. Newer data indicate, however, that compounds exist in metal–hydrogen systems.

Accurate measurement of the dissociation pressures of the hydrides of lanthanum, cerium, praseodymium, neodymium, and gadolinium [32] has confirmed, and extended to other elements, the suggestion made by Zhukov in 1912 regarding the formation of cerium dihydride [47]. X-ray analysis also confirms the existence of these compounds and their coexistence with metal in the range $M-MH_2$ [31]. Some properties of these hydrides are given in Table 8.

Cerium dihydride is stable up to 900°–1000°, and starts to decompose rapidly only after fusion at 1060°–1080°. [20]

From the point of view of the relationship between a compound and a solid solution, the phases of variable composition in the range $MH_2 - MH_3$ are of particular interest. In the case of cerium, lanthanum, neodymium, and praseodymium, measurement of the dissociation pressure and X-ray analysis has shown the presence in this range of a continuous series of solid solutions whose density increases regularly with increase in the hydrogen content.

Comparison of this fact with data for the chemical reactivity of the cerium hydrides CeH_2 and CeH_3, of which the former exhibits more marked metallic character, while the latter is more reactive towards water, leads inevitably to the idea that there is a gradual change in the nature of the chemical bond within the limits of the solid phase CeH_2-CeH_3, i.e. to the suggestion that two valency forms of cerium exist together in equilibrium. The views of Daou and Auphassorho [56,58] are of interest in this connection.

The authors consider that the redistribution of hydrogen in the octahedral holes, which takes place in this range, leads to an increase in the ionic character of the bond, as in the salt-like hydrides. Auphassorho considers that this

TABLE 6. Radius of the hydride anion in the intermediate hydrides [92].

Hydride	M–H distance, Å	Cationic radius, Å	Oxidation state of cation	Correction for coordination number	H radius, Å
TiH_2	1.93	0.60	4+	0.08	1.25
ZrH_2	2.09	0.77	4+	0.08	1.24
LaH_2	2.45	1.04	3+	0.08	1.33
CeH_2	2.42	1.02	3+	0.08	1.32
PrH_2	2.39	1.00	3+	0.08	1.31
NdH_2	2.37	0.99	3+	0.08	1.30
SmH_2	2.33	0.97	3+	0.08	1.28
GdH_2	2.30	0.95	3+	0.08	1.27
AcH_2	2.46	1.11	3+	0.08	1.27
ThH_2	2.41	0.99	4+	0.08	1.34
PaH_2	2.32	0.90	5+	0.19	1.23
UH_2	2.32	0.86	6+	0.19	1.27
PuH_2	2.32	0.90	4+	0.08	1.34

TABLE 7. Radius of the hydride anion in the alkali metal hydrides [92].

Hydride	M–H distance, Å	Cationic radius, Å	Radius of H^- ion, Å
CsH	3.19	1.67	1.52
RbH	3.02	1.48	1.54
KH	2.85	1.33	1.52
NaH	2.44	0.98	1.46
LiH	2.05	0.68	1.37

TABLE 8. Properties of the dihydrides of certain rare-earth metals.

Element	Heat of formation of dihydride, kcal/mole	Lattice parameter, Å	Density, g/cm³	Relationship between dissociation pressure and temperature
La	49.7	5.667	5.14	$\log p = 10.758 - 10858/T$
Ce	33.9	5.581	5.43	$\log p = 7.708 - 7417/T$
Pr	47.8	5.517	5.65	$\log p = 10.229 - 10446/T$
Nd	44.8	5.470	5.94	$\log p = 9.370 - 9796/T$
Sm	—	5.376	6.52	—
Gd	46.9	5.303	7.08	—

is confirmed by the formation of a δ-phase in the cerium–hydrogen system, in which the hydrogen is distributed only in the octahedral holes, leading to a considerable contraction in the metal lattice, i.e. to a phenomenon characteristic of the formation of an ionic M–H bond.

Thus the solid phase CeH_2–CeH_3 in the Ce–H system is an extremely interesting example of a berthollide phase[2,3]. Within the range of homogeneity of this phase, we have a continuous transition from the compound CeH_2 with greater metallic-bond character (the hydrogen atoms arranged in the tetrahedral holes of the face-centred cerium lattice) to the compound CeH_3, with greater ionic-bond character (the hydrogen atoms arranged in both tetrahedral and octahedral holes in the lattice).

Further interesting data are provided by the gadolinium–hydrogen system[70]. Unlike the systems described above, this shows the formation of a new phase GdH_3, with hexagonal lattice, in the GdH_2–GdH_3 range. This difference is evidently explained by the fact that gadolinium trihydride, unlike the trihydrides of the other rare-earth metals, does not form solid solutions with the dihydride.

In spite of the fact that study of the dissociation pressure and X-ray analysis in the case of cerium, lanthanum, neodymium, and praseodymium give no direct indication of the existence of the trihydrides of these elements, there is indirect proof that such compounds exist. Thus the existence of the compound CeH_3 is suggested by the formation of the double hydride $Ce(AlH_4)_3$. At the same time, a fundamental difference between the trihydride CeH_3 and hydrides of composition intermediate between CeH_2 and CeH_3 is indicated by the definite and fairly wide range of temperature and pressure within which a hydride of definite stoichiometric composition is formed[8,20].

The data for the rare-earth elements cerium, lanthanum, neodymium, praseodymium, samarium, gadolinium, etc. may thus be taken as proving the existence of hydrides of composition MH_2 and MH_3.

While the rare-earth metals have many properties in common, such as the ability to combine directly with hydrogen with the evolution of heat, to form phases of variable composition, etc., certain individual features can also be distinguished — for example, the appearance of a trihydride of hexagonal structure in the case of samarium and gadolinium. It is also reported that gadolinium forms a compound Gd_2H_3. A more marked difference is shown by europium and ytterbium hydrides, whose properties are similar to those of the alkaline-earth compounds.

The lack of attention paid to these compounds is apparent. Thus, as recent work of Auphassorho[56] shows, even in the case of cerium, which has been most studied, new evidence has been obtained for the existence of a hydride of approximate composition CeH, with properties similar to those of the salt-like hydrides.

Since the reaction of most of the other rare-earth elements with hydrogen has been studied in even less detail than in the case of cerium, much new and interesting material should be obtained in further studies, particularly by physicochemical methods. Similarly the ability of these elements to form double boro- and aluminohydrides has so far received little attention. Further investigation of the individual properties of the rare-earth hydrides, double hydrides, and their derivatives appears promising, both as regards the appearance of individual characteristics in the separate members of the family and also as regards their practical applications.

CONCLUSION

Experiment shows that in rare-earth metal–hydrogen systems, compounds of constant composition and phases of intermediate composition exist in equilibrium. The solid phases MH_2–MH_3, which have been studied for cerium and lanthanum, are of particular interest in establishing the relationships observed in the transition between chemical compound and solution. In accordance with the views of Kurnakov on berthollide phases, there is in these phases a mobile equilibrium between several valency forms of the rare-earth metal. The experimental study of the composition and properties of the hydrides also reveals the individual features of the separate rare-earth metals, which on the whole resemble one another very closely.

Certain properties of the rare-earth hydrides, such as the thermal stability of the dihydrides and the change in the nature of the chemical bond in the MH_2–MH_3 range, indicate that it should be possible to use these compounds to advantage in special fields of metallurgy, certain types of synthesis by heterogeneous catalysis, and in the technology of semiconductor materials.

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THE CHEMISTRY OF QUINUCLIDINE DERIVATIVES

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INTRODUCTION

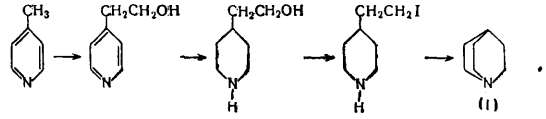
Quinine is one of the oldest and most widely known medicinal substances and its structure and synthesis have been investigated by workers in many countries.

A nitrogen-containing bicyclic system, quinuclidine[1--azabicyclo-(2,2,2)-octane] is a component part of the quinine molecule and of other quinine alkaloids. Up to the last decade little was published on quinuclidines for lack of methods of preparation of these compounds. Recent developments have made it possible to prepare various mono- and disubstituted quinuclidines, some of them with marked pharmacological or chemotherapeutic activity adding further importance to investigations of quinuclidine synthesis.

QUINUCLIDINE

The starting materials for the synthesis of quinuclidine and its derivatives are pyridines, dihalogenoalkylamines, or aliphatic trihalides of suitable structure.

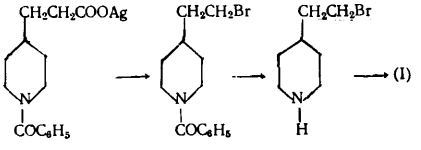
Quinuclidine (I) was first synthesised in 1909 by Löffler and Stiezel[1] according to the scheme



4-Methylpyridine reacts with formaldehyde to form, among other substances, 4-(β-hydroxyethyl)pyridine which, on reduction by the Vyshnegradskii–Ladenburg method and subsequent replacement of the hydroxy group by iodine using hydriodic acid, gives 4-(β-iodoethyl)piperidine; the latter is converted to quinuclidine by dilute alkali. The authors failed to isolate quinuclidine in a pure state. The picrate had m.p. 209°–211°, the base itself being a non-crystallising oily substance.

Later, Meisenheimer[2] followed the same route and obtained quinuclidine in the form of colourless crystals, m.p. 154°, yielding a picrate, m.p. 275°. His physical constants were confirmed by others[3-7] who synthesised quinuclidine by various methods. The method mentioned above had the disadvantage of a low yield of 4-(β-hydroxyethyl)-pyridine (1.5–2%) and consequently a very low yield of quinuclidine (0.4%). However, if 4-methylpyridine is heated with paraformaldehyde at 160°,[8] the yield of the intermediate rises to 48% and considerably higher overall yields of quinuclidine are therefore attainable.

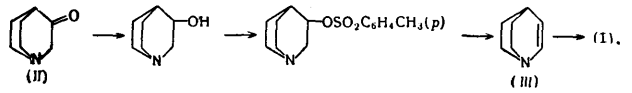
Another method of quinuclidine synthesis was described in 1947:[5]



The silver salt of 1-benzoyl-4-(β-carboxyethyl)piperidine is converted to a bromo-compound (by treatment with bromine in carbon tetrachloride), which gives quinuclidine on hydrolysis of the benzoyl group and subsequent cyclisation with dilute sodium hydroxide.

Clemo and Metcalfe[6] prepared quinuclidine by reducing 3-quinuclidone (II) (for synthesis see p. 42) according to Kishner or Clemmensen. Quinuclidine was isolated as the picrate without mention of the yield.

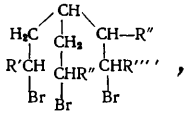
Grob et al.[7] prepared quinuclidine via 1-azabicyclo--(2,2,2)-2-octene (dehydroquinuclidine) (III) starting with 3-quinuclidone:



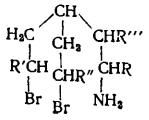
3-Hydroxyquinuclidine, obtained by reduction of (II), was converted to the tosyl ester from which (III) was obtained on heating with sodium ethoxide. Compound (III) is a colourless liquid which solidifies to volatile hygroscopic crystals on cooling; it absorbs hydrogen readily to give quinuclidine. Addition of hydrogen bromide to (III) gives 3-bromoquinuclidine. This substance and the corresponding chloro derivative [isolated with (III) on heating 3-hydroxyquinuclidine with thionyl chloride] are reduced to quinuclidine in the presence of Raney nickel catalyst.

In 1951 Wawžonek[9] reported the preparation of quinuclidine by irradiation of 1-halogeno-4-ethylpiperidines in 85% sulphuric acid with ultra-violet light. This was refuted by Lukeš and Furles[10] who showed that the compound formed was 2-methyl-1-azabicyclo-(2,2,1)-heptane.

Prelog[11] approached the synthesis of quinuclidine from another direction. The methods he developed are based on the action of ammonia under pressure at 100°–120° on aliphatic tribromides of the general formula

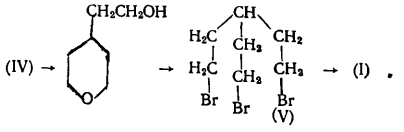


or on "double intramolecular alkylation" brought about by alkali treatment of dibromoalkylamines of the type



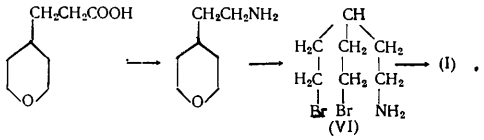
The appropriate dibromoalkylamines and tribromoalkanes were obtained from tetrahydropyrans[12-14], the most widely used compound being tetrahydropyran-4-acetic acid prepared from 4-hydroxymethyltetrahydropyran or from γ-pyrone.

The conversion of the ethyl ester of tetrahydropyran-4--acetic acid (IV) to quinuclidine is represented by the following scheme:



The ester (IV) is reduced by sodium and alcohol to 4-(β--hydroxyethyl)tetrahydropyran which is converted by fuming HBr to the tribromoalkane (V) which yields quinuclidine on heating with a methanolic ammonia. Compound (V) has also been synthesised from acetone dicarboxylic ester via the trimethyl ester of methanetriacetic acid[4].

The dibromoalkylamine (VI) is prepared by converting tetrahydropyran-4-acetic acid to β-(4-tetrahydropyranyl)-propionic acid which undergoes the Schmidt reaction to give 4-(β-aminoethyl)tetrahydropyran. This, treated with hydrobromic acid, yields compound (VI). The latter forms quinuclidine when treated with sodium hydroxide.

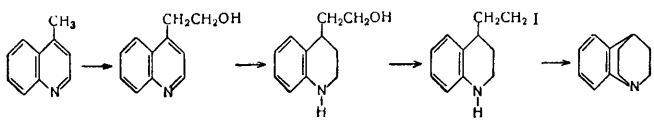


The methods of preparation of quinuclidine from tribromoalkanes and dibromoalkylamines are inferior to synthesis from 4-(β-hydroxyethyl)pyridine and 3-quinuclidone in respect to the number of steps and the yield.

Quinuclidine is a volatile crystalline substance which forms salts with mineral acids and alkyl halides. It is chemically inert to a number of reagents: it remains unchanged after prolonged heating with concentrated acids (H_2SO_4, HNO_3, HCl) and is not oxidised by potassium permanganate[2]. It is dehydrogenated to 4-ethylpyridine by heating in a sealed vessel at 300°–350° in the presence of catalysts (palladised charcoal or selenium)[15]. The chemical stability and high melting point of quinuclidine (158°) are due to the high symmetry of the molecule which makes the strain in the bicyclic system very slight[2,16].

When 1-methyl quinuclidine quaternary bases undergo the Hofmann reaction[4], 1-methyl-4-vinylpiperidine, 1-methyl-4-(β-hydroxyethyl)piperidine and quinuclidine are formed.

Of the condensed systems containing quinuclidine, benzo- and dibenzoquinuclidine have been described, the former by Meisenheimer[2] who prepared it from 4-methylquinoline by the same method as that used for quinuclidine.

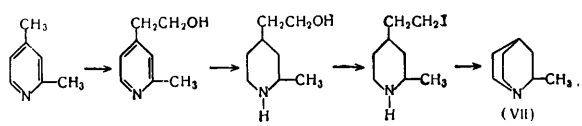


Benzoquinuclidine is a crystalline substance, m.p. 68°–69°, which is stable to acid potassium permanganate and does not undergo diazo-coupling with diazotised *p*-nitroaniline[17]. Dibenzoquinuclidine was prepared by Krogt and Wepster[18] from 9-methylacridine in a similar way.

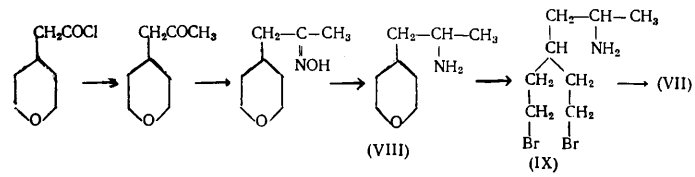
The pharmacological activity of quinuclidine has not been adequately investigated; its hydrochloride is known to have strong hypotensive properties and to relax smooth muscle[19].

2-Substituted Quinuclidines

The simplest member of this group is 2-methylquinuclidine (VII) which was synthesised by Winterfeld in 1930 from 2,4-dimethylpyridine according to a scheme similar to the one described above for the preparation of quinuclidine:



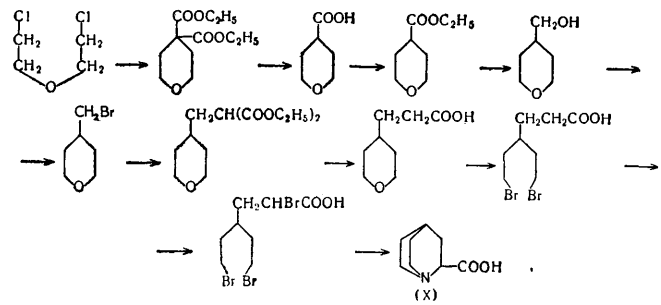
2-Methylquinuclidine was also prepared by Prelog[14] from tetrahydropyran-4-acetic acid. The acid chloride reacts with the methyl Grignard reagent to give 4-acetonyltetrahydropyran. The oxime of the latter is reduced to the amine (VIII) and the pyran ring is then opened by heating with hydrobromic acid. The compound (IX) thus formed is converted to 2-methylquinuclidine by a double intramolecular alkylation:



2-Ethylquinuclidine was prepared similarly from 1-(4-tetrahydropyranyl)-2-butanone[14].

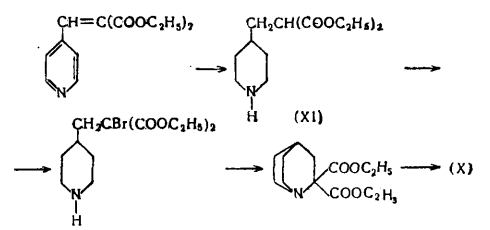
Quinuclidine-2-carboxylic acid (X) is of considerably greater interest. It is a key substance in the preparation of most 2-substituted quinuclidines; a considerable amount of published work deals with its synthesis.

The acid was first synthesised by Prelog and Gerkovnikov[21] in 1937 as follows:



Bis-β-chloroethyl ether reacts with malonic ester to give 4,4-diethoxycarbonyltetrahydropyran which is subject to successive hydrolysis, partial decarboxylation and esterification. The ethyl tetrahydropyran-4-carboxylate obtained is reduced by the Bouveault method; the hydroxyl group is replaced by a bromine atom and the side-chain is lengthened by two carbon atoms using the malonic ester synthesis. Subsequent opening of the pyran ring by heating under pressure with hydrobromic acid, introduction of bromine adjacent to the carboxyl group, and cyclisation of the product, gives (X) as colourless crystals, m.p. 280°. This synthesis consists of ten steps and the overall yield of (X) is only 4%.

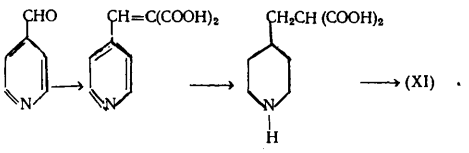
A simpler method for the preparation of (X) was developed in 1953[22]:



When the β-picoline fraction, free from 2,6-dimethylpyridine, is heated with mesoxalic ester and acetic anhydride for 9 h at 90°, 4-(β,β-diethoxycarbonylvinyl)pyridine is formed. This is hydrogenated in anhydrous alcohol over platinum and then treated with bromine in chloroform solution to give 4-(β,β-diethoxycarbonyl-β-bromoethyl)piperidine which, when heated with pyridine, cyclises to 2,2-diethoxycarbonylquinuclidine. The latter is hydrolysed and partially decarboxylated by boiling for 8 h with concentrated hydrochloric acid yielding (X) as the hydrochloride which melts with decomposition at 292°–294°. The synthesis is accomplished in 5 steps and the total yield is 30%.

Various routes to the intermediate product (XI) in the above synthesis of quinuclidine-2-carboxylic acid have

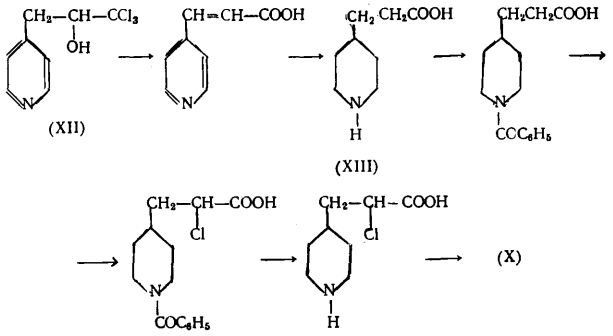
been studied[23]. It was shown that (XI) could be prepared from 4-formylpyridine and malonic ester or malonic acid:



Condensation of 4-formylpyridine with malonic acid in glacial acetic acid gives 4-(β,β-dicarboxylvinyl)pyridine which is very unstable to heat and must first be hydrogenated to the piperidine derivative which is then esterified.

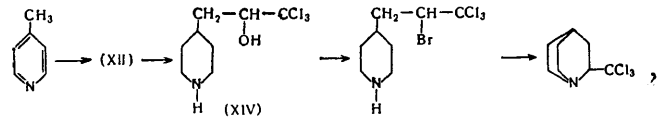
Compound (XI) can also be obtained by the Knoevenagel reaction between 4-formylpyridine and malonic ester and subsequent catalytic reduction of 4-(β,β-diethoxycarbonylvinyl)pyridine. Both variants have the disadvantage that low yields are obtained in the preparation of 4-formylpyridine (12.7% from γ-picoline).

A new synthesis for (X) was proposed by Renk and Grob in 1954[24]:



The starting material is γ-picoline which condenses with chloral in the presence of piperidine to form a chloral derivative (XII). Saponification of (XII) with alcoholic alkali gives 4-(β-carboxyvinyl)pyridine, the potassium salt of which is catalytically (Ni) reduced in aqueous solution to form 4-(β-carboxyethyl)piperidine (XIII). The N-benzoyl derivative of (XIII) is chlorinated with sulphuryl chloride, the N-benzoyl group is saponified by boiling with concentrated HCl, and the product is cyclised by heating with aqueous sodium hydroxide. This synthesis contains 7 steps and the overall yield is 26%.

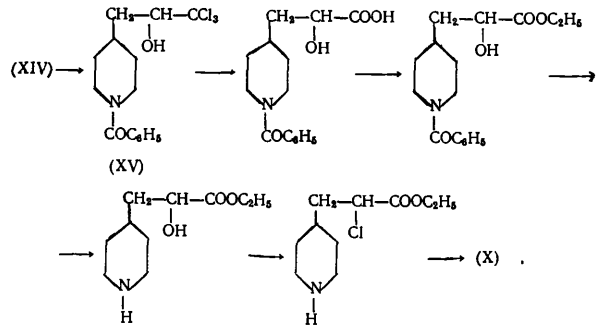
Investigation of other syntheses of (X) from γ-picoline[25] disclosed certain peculiarities in the behaviour of the intermediate compounds. Thus when the following scheme is employed:



the reduction of (XII) with platinum catalyst to (XIV) goes smoothly but substitution of halogen for the hydroxy group in (XIV) runs into difficulties. The reaction does not occur with thionyl chloride or phosphorus halides; however, heating with 68% hydrobromic acid at 120° gives a 40% yield of 4-(γ,γ,γ-trichloro-β-bromopropyl)piperidine. This yields a small amount of 2-trichloromethylquinuclidine on being treated with aqueous sodium carbonate.

During saponification of (XIV), β-(4-piperidyl)lactic acid is formed, esterification of which gives a polymeric ester.

The use of the N-benzoyl derivative (XV) gives monomeric ethyl β-(4-piperidyl)lactate which can be converted to (X) by substituting halogen for the hydroxy group.

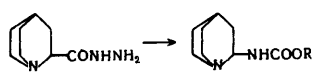


It was found in the course of this synthesis that substitution of chlorine for the hydroxy group in the ethyl β-(4-piperidyl)lactate (using thionyl chloride) only occurred to the extent of 25%; the reaction mixture consisted mainly of the starting material. The overall yield of (X) is therefore considerably lower than in the reaction mentioned above, which so far is the most convenient method of preparing (X).

Quinuclidine-2-carboxylic acid serves as starting material for the preparation of almost all the 2-substituted quinuclidines described.

Bouveault reduction, or treatment with lithium aluminium hydride, of the ethyl ester of (X), gives quinuclidine-2-carbinol. This carbinol is converted by thionyl chloride to 2-chloromethylquinuclidine[14] and by hydrobromic acid (under pressure) to 2-bromomethylquinuclidine[26]. The ethyl ester of (X) with phenyl magnesium bromide gives a good yield of diphenylquinuclidyl-2-carbinol[14]; the amide of (X), treated with thionyl chloride under pressure, yields 2-cyanoquinuclidine[22]. The Borodin reaction on (X) produces 2-bromoquinuclidine in 16% yield[22].

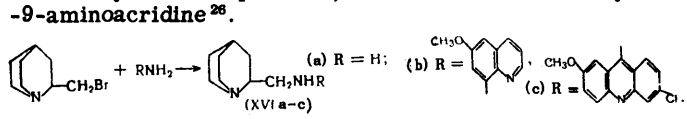
The hydrazide and some of its derivatives can be obtained from the ethyl ester of (X)[27]. The Curtius reaction was applied to the hydrazide and rearrangement of the azide of (X) occurred normally with formation of ethyl N-(2-quinuclidyl)urethane which is an acylated 2-aminoquinuclidine:



(where R = C_2H_5 or iso-C_5H_{11}). However, when attempts are made to isolate 2-aminoquinuclidine (an asymmetrically substituted diaminomethane) a molecule of ammonia is eliminated and the dehydroquinuclidine formed polymerises[28].

Large numbers of substituted 2-aminomethylquinuclidines have been synthesised, in a search for synthetic analogues of quinine alkaloids, and as ganglion blocking agents.

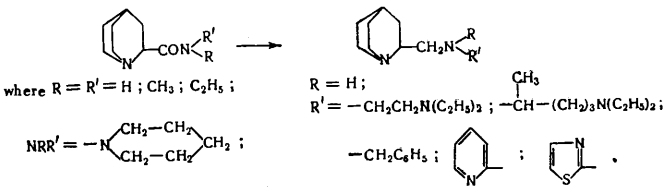
The first members of this series, 2-aminomethylquinuclidine (XVIa), 8-(2-quinuclidylmethylamino)-6-methoxyquinoline (XVIb), and 6-chloro-2-methoxy-9-(2-quinuclidylmethylamino)acridine (XVIc), were prepared by reaction of 2-bromomethylquinuclidine with ammonia, 6-methoxy-8-aminoquinoline, and 6-chloro-2-methoxy-9-aminoacridine[26].



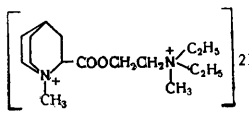
Studies of the chemotherapy of (XVI b and c) showed that these compounds were considerably more active than quinine in trials on canaries infected with *Plasmodium relictum* [29].

9-(2-Quinuclidylmethylamino)acridine and 4-(2-quinuclidylmethylamino)-6-methyoxyquinoline were synthesised later by reaction of 2-aminomethylquinuclidine with 9-phenoxyacridine and 6-methoxyquinoline-4-sulphonic acid [30] respectively.

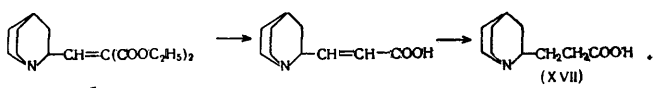
Substituted 2-aminomethylquinuclidines can be easily obtained by reduction of the corresponding quinuclidine-2--carboxamides with lithium aluminium hydride. A number of compounds were thus obtained with yields of 70–80% [31].



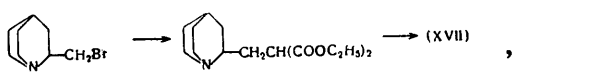
Some members of this series have high ganglion blocking activity, the most marked being that of 2-(β-diethylaminoethyl)aminomethylquinuclidine [32]. Such activity is also present in the dimethiodide of diethylaminoethyl quinuclidine-2-carboxylate which is used under the name of "Dioxin" for the treatment of hypertensive disease [33].



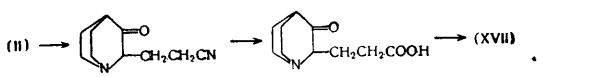
2-Formylquinuclidine is of considerable interest for the synthesis of 2-substituted quinuclidines; it was obtained by reduction of the N-methylanilide of quinuclidine-2--carboxylic acid by lithium aluminium hydride (31% yield) [34]. When 2-formylquinuclidine is condensed with malonic ester by the Knoevenagel method, quinuclidyl-2-methylenemalonic ester is formed. This is converted by boiling concentrated hydrochloric acid into β-(2-quinuclidyl)acrylic acid, which is easily reduced in the presence of Raney nickel to β-(2--quinuclidyl)propionic acid (XVII):



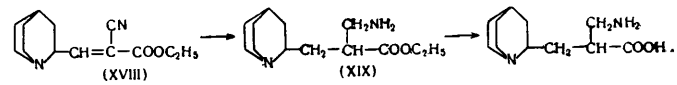
Compound (XVII) has also been prepared by condensing 2-bromomethylquinuclidine with sodium malonic ester and boiling the product with hydrochloric acid [35]:



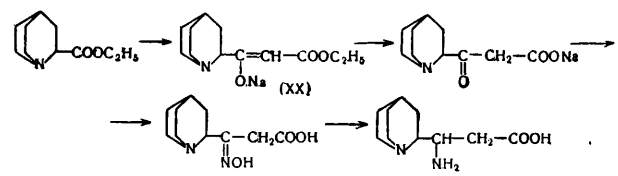
and by cyanethylation of 3-ketoquinuclidine (II), saponification of the nitrile group, and Kishner reduction of the resulting β-(3-keto-2-quinuclidyl)propionic acid [36]:



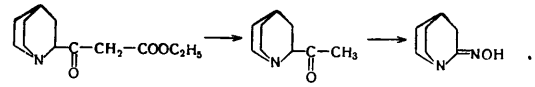
Condensation of 2-formylquinuclidine with cyanacetic ester gives α-cyano-β-(2-quinuclidyl)acrylic ester (XVIII); this is catalytically reduced to the aminoester (XIX) which is hydrolysed in the usual way to α-aminomethyl-β-(2--quinuclidyl)propionic acid [37]:



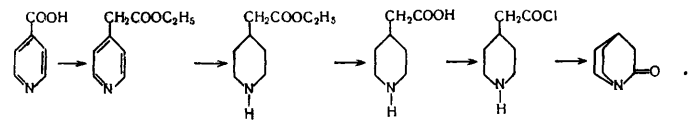
Claisen condensation of the ethyl ester of quinuclidine-2--carboxylic acid with ethyl acetate gives the ethyl ester of β-(2-quinuclidyl)-β-ketopropionic acid, isolated as the sodium derivative of the enolic form, which is but slightly soluble in water (XX). This compound reacts with water (24 h at room temperature) to form the sodium salt of β-(2-quinuclidyl)-β-ketopropionic acid, the oxime of which is readily reduced catalytically to β-(2-quinuclidyl)-β--aminopropionic acid [37]:



Hydrolysis and decarboxylation of the ethyl β-(2-quinuclidyl)-β-ketopropionate is effected by concentrated hydrochloric acid and gives 2-acetylquinuclidine. Treatment of this with isoamyl nitrite in the presence of sodium ethoxide yields 2-quinuclidone oxime:

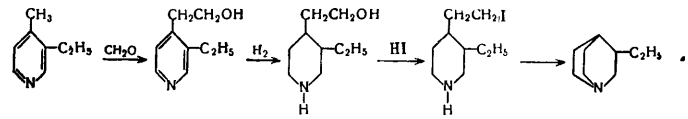


The ketone was also prepared from isonicotinic acid according to the following scheme [38]:



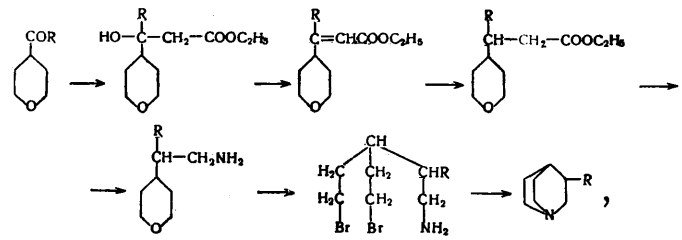
3-Substituted Quinuclidines

Derivatives of pyridine are generally used for the preparation of these compounds. Thus in 1904 Koenigs [39,40] prepared 3-ethylquinuclidine from 3-ethyl-4-methylpyridine as follows:



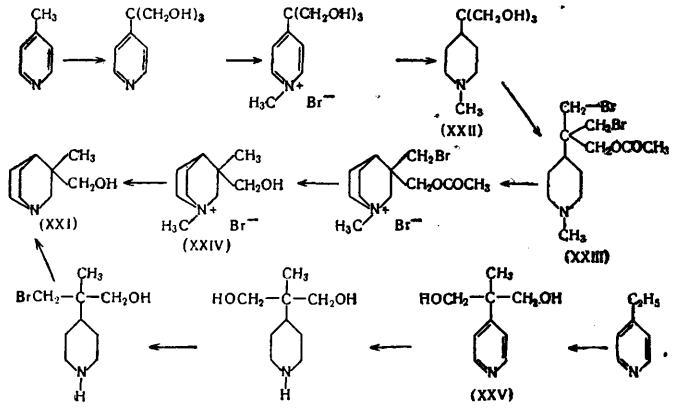
As already mentioned, Meisenheimer [2] used the same scheme for the preparation of quinuclidine and Winterfeld [20] for that of 2-methylquinuclidine.

Prelog [14] prepared 3-methyl- and 3-ethylquinuclidine from tetrahydropyrans with branched-chain substituents in the 4-position:



where R = CH_3; C_2H_5.

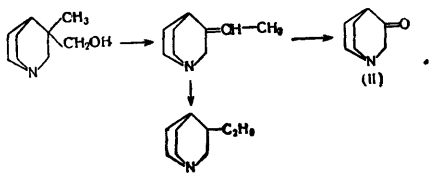
A number of 3-substituted quinuclidines were prepared by Lukeš and Ernest from pyridine derivatives. These authors set out to synthesise 3-vinylquinuclidine from 3-methyl-3-hydroxymethylquinuclidine (XXI). Compound (XXI) had been prepared by two methods: from 4-methyl- and 4-ethylpyridine[41-43] according to the following routes:



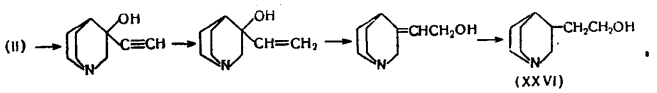
In the first scheme 4-[tri(hydroxymethyl)methyl]pyridine, obtained from 4-methylpyridine and formaldehyde, is converted to the methobromide and then reduced to 1-methyl-4-[tri(hydroxymethyl)methyl]piperidine (XXII). Prolonged heating of (XXII) with hydrobromic acid in acetic acid gives the dibromide (XXIII) which is converted by boiling alcohol into 3-bromomethyl-3-acetoxymethylquinuclidine methobromide. This is reduced to 3-methyl-3-hydroxymethylquinuclidine methobromide (XXIV). Heating (XXIV) under vacuum gives the compound (XXI).

The second and shorter route uses 4-ethylpyridine as the starting material which reacts with formaldehyde to give the glycol (XXV). The hydrobromide of this glycol is hydrogenated to the piperidine stage, one hydroxy group is replaced by bromine, and the product is cyclised to give (XXI) in overall yield of 57%. The conversion of 4-ethylpyridine to (XXI) through 4-(2-methyl-1,3-dihydroxy-2-propyl)pyridine described later[44], has no advantage over the above method.

Compound (XXI) was subjected to dehydration which cannot occur without a retropinacoline rearrangement. It was intended to make use of this in the preparation of 3-vinylquinuclidine, but 3-ethylidenequinuclidine (oxidised to 3-quinuclidone and reduced to 3-ethylquinuclidine), was isolated instead:

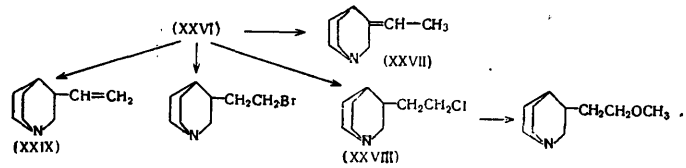


3-Vinylquinuclidine was subsequently prepared from 3-(β-hydroxyethyl)quinuclidine (XXVI)[45] obtained from 3-quinuclidone via 3-hydroxy-3-ethynylquinuclidine as follows:



Reduction of 3-hydroxy-3-ethynylquinuclidine with the calculated amount of hydrogen gives 3-hydroxy-3-vinylquinuclidine which rearranges when heated with hydrogen bromide in glacial acetic acid to 3-(β-hydroxyethylidene)-quinuclidine, isolated as two stereoisomers. When this compound is reduced over a platinum catalyst 3-(β-hydroxyethyl)quinuclidine is formed.

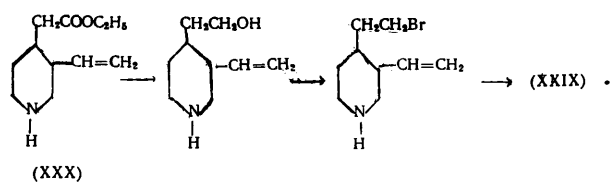
When (XXVI) is dehydrated with phosphorus pentoxide to obtain 3-vinylquinuclidine, the double bond shifts to the semicyclic position and 3-ethylidenequinuclidine (XXVII) is formed. Compound (XXVI) reacts with concentrated hydrochloric acid at 180° to give 3-(β-chloroethyl)quinuclidine (XXVIII) and (XXVII); at lower temperatures (100°–150°) the only product is (XXVIII).



Replacement of the β-hydroxy group in (XXVI) by a bromine atom (HBr) gives 3-(β-bromoethyl)quinuclidine which easily forms the quaternary polymer. When (XXVIII), which has less tendency to polymerise, is treated with potassium hydroxide in methanol the product is 3-(β-methoxyethyl)quinuclidine. Heating (XXVIII) with aqueous potassium hydroxide leads to intramolecular alkylation.

Ernest[47] obtained 3-vinylquinuclidine (XXIX) mixed with 3-ethylidenequinuclidine by dehydrating (XXVI) with phthalic anhydride and benzenesulphonic acid. Racemic (XXIX) was isolated from this mixture by repeated recrystallisation of the styphnates.

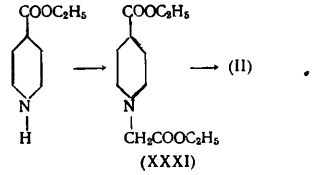
Optically active 3-vinylquinuclidine was prepared by Lukeš and Galik[48] from the ethyl ester of meroquinene (XXX) obtained from naturally-occurring cinchonine[49]:



The ester (XXX) is reduced with lithium aluminium hydride to 3-vinyl-4-(β-hydroxyethyl)piperidine, the hydroxy group is replaced by bromine (HBr), and the bromide is cyclised to 3-vinylquinuclidine.

The synthesis of 3-quinuclidone (II) was a milestone in the preparation of quinuclidine derivatives. This compound served as starting material for the preparation of many 2- and 3-monosubstituted and some 2,3-disubstituted quinuclidines.

Clemo[6] first synthesised 3-quinuclidone as follows:

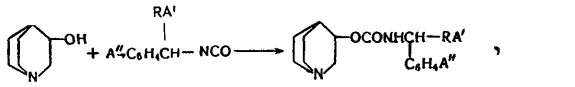


Ethyl isonipecotinate reacts with ethyl chloracetate in the presence of potassium carbonate to give ethyl 1-ethoxycarbonylmethylisonipecotinate (XXXI). Cyclisation of the diester (XXXI) with potassium in toluene, followed by saponification and decarboxylation, leads to 3-quinuclidone.

Sternbach and Kaiser[50], who synthesised (II) in 1952, modified Clemo's scheme only as regards the preparation of the diester. Instead of alkylating ethyl isonipecotinate they reduced the ethoxycarbonylmethobromide of methyl isonicotinic acid to methyl 1-ethoxycarbonylmethylisonipecotinate. The latter, as in Clemo's scheme, was converted to (II) in 37–43% yield. The yield was increased to 82% by using a potassium alkoxide instead of metallic potassium[36].

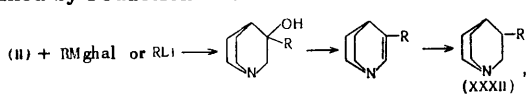
The presence of a reactive keto group in compound (II) made it possible to synthesise various 3-substituted quinuclidines, e.g. the oxime reduced over platinum gives 3-aminoquinuclidine, and reduction of (II) itself gives 3-hydroxyquinuclidine which can be converted by hydrobromic acid to 3-bromoquinuclidine[50]. Esterification of 3-hydroxyquinuclidine with tropic, diphenylacetic, benzilic, fluorenecarboxylic and *o*-acetylmandelic acids gives esters with atropine-like and antispasmodic properties. The most active of these, 3-diphenylacetoxyquinuclidine, is 20 times as active as atropine[51–54]. The esters formed by the above acids with 3-methyl-3-hydroxyquinuclidine have no antispasmodic activity[52].

Urethanes (3-carbamoxyquinuclidines) were also synthesised from 3-hydroxyquinuclidine and isocyanates in order to investigate their biological properties[55]:



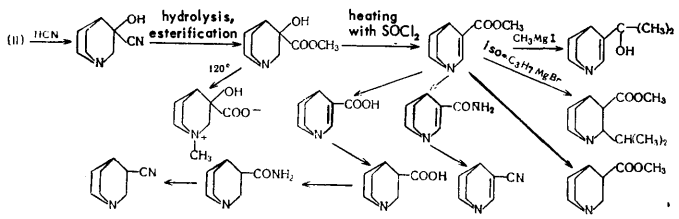
where A' and A" = H, halogen, NO_2, alkoxyl, or alkyl, and R = C_6H_5 or C_6H_{11}.

3-Quinuclidone has been used for the synthesis of 3-aryl- and 3-alkylquinuclidines (XXXII). Organo magnesium or lithium compounds form the 3-hydroxy-3-aryl- and -alkylquinuclidines which are converted to 3-aryl- and 3-alkyl-1-azabicyclo-(2,2,2)-2-octenes by thionyl chloride, sulphuric acid, or acid chlorides. The compounds (XXXII) are then obtained by reduction[7,56].

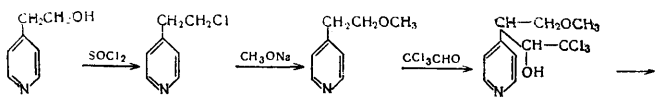


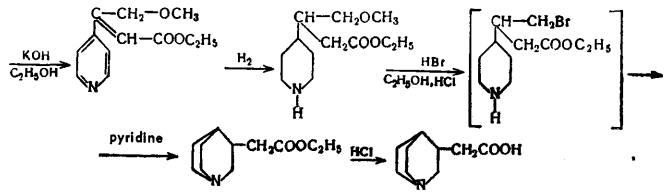
where R = C_6H_5, *p*-$C_6H_4N(CH_3)_2$, *p*-$C_6H_4OCH_3$, *p*-C_6H_4OH, or CH_3.

Grob and Renk[57] used the reactive 3-quinuclidone for the synthesis of quinuclidine-3-carboxylic acid and a number of its derivatives; the following route was adopted:

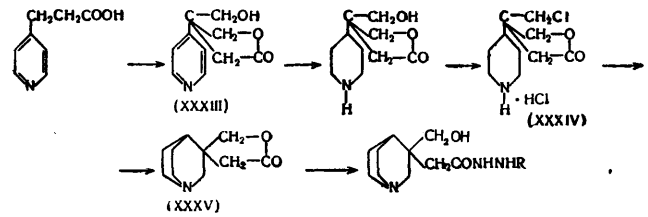


The next homologue, quinuclidine-3-acetic acid[58] was prepared from 4-(β-hydroxyethyl)pyridine, itself obtained by reaction of 4-methylpyridine with formaldehyde:





The synthesis of 3-hydroxymethyl-3-carboxymethylquinuclidine lactone, a derivative of quinuclidine-3-acetic acid, has been described[59]:

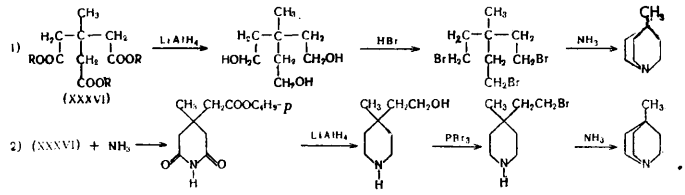


When β-(4-pyridyl)propionic acid or its esters are heated with formalin, the lactone of β,β-di(hydroxymethyl)-β-4-pyridylpropionic acid (XXXIII) is formed. This compound is reduced in alcohol or hydrochloric acid over platinum to the corresponding piperidine which is converted by thionyl chloride to β-chloromethyl-β-(4-piperidyl)-γ-butyrolactone hydrochloride (XXXIV). The base isolated on treating (XXXIV) with one equivalent of alcoholic potassium hydroxide is converted by pyridine to the lactone of 3-hydroxymethyl-3-carboxymethylquinuclidine (XXXV). This lactone forms a hydrazide and a phenylhydrazide with hydrazine hydrate and phenylhydrazine respectively. Benzylamine, piperidine, and decylamine do not open the lactone ring.

4-Substituted Quinuclidines

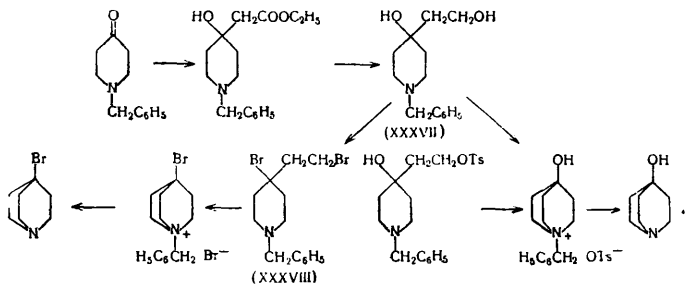
These compounds are the least well investigated of the monosubstituted derivatives of quinuclidine. The synthesis of 4-methyl-, 4-hydroxy-, and 4-bromoquinuclidines and of quinuclidine-4-carboxylic acid and some of its derivatives has been described.

Lukeš and Ferles[60] prepared 4-methylquinuclidine by two methods:



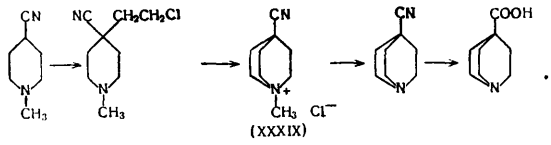
4-Hydroxy- and 4-bromoquinuclidine[61] have been prepared from 1-benzyl-4-piperidone. This was converted by the Reformatsky reaction to 1-benzyl-4-hydroxy-4-ethoxycarbonylmethylpiperidine which was reduced by lithium aluminium hydride to the diol (XXXVII) whose monotosyl (Ts) derivative was cyclised by heating in benzene to a quaternary salt of 4-hydroxyquinuclidine. The latter is reduced over palladised charcoal to 4-hydroxyquinuclidine.

When the diol (XXXVII) is heated with hydrobromic acid it is converted to the dibromide (XXXVIII) which is cyclised to 1-benzyl-4-bromoquinuclidinium bromide. On reduction, this yields 4-bromoquinuclidine[62].



(XXXVII) (XXXVIII)

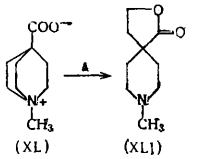
Quinuclidine-4-carboxylic acid was synthesised by Grob and Renk[63] as follows:



(XXXIX)

1-Methyl-4-cyanopiperidine reacts with 1,2-dichloroethane in the presence of sodium phenate to give 1-methyl-4--cyano-4-(β-chloroethyl)piperidine which cyclises to 4-cyanoquinuclidine methochloride (XXXIX). When the latter is heated under vacuum to 260°–270° methyl chloride is eliminated and 4-cyanoquinuclidine is formed. This is hydrolysed to quinuclidine-4-carboxylic acid which does not melt at 370° and presumably exists as a zwitterion.

4-Cyanoquinuclidine methochloride can be hydrolysed to a crystalline betaine (XL):

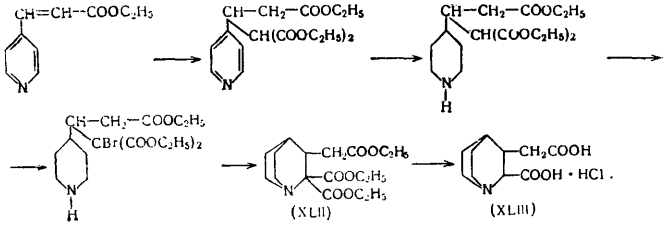


(XL) (XLI)

Heating above 250° transforms (XL) into an isomeric base which is considered to be the lactone (XLI) of 1-methyl-4--(β-hydroxyethyl)piperidine-4-carboxylic acid. The following have been prepared from quinuclidine-4-carboxylic acid: various esters by treating the acid chloride with alcohols, 4-hydroxymethylquinuclidine by reducing these esters with lithium aluminium hydride, 4-formylquinuclidine by oxidation of this alcohol with potassium dichromate, and 4-methylquinuclidine by reduction of 4-formylquinuclidine semicarbazone by the Wolf–Kishner method.

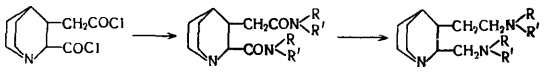
2,3-Disubstituted Quinuclidines

Published data on the preparation of various members of this group are based on 3-carboxymethylquinuclidine-2--carboxylic acid[64] obtained according to the following scheme:



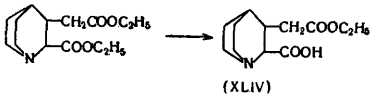
(XLII) (XLIII)

Ethyl of β-(4-pyridyl)acrylate undergoes a Michael condensation with malonic ester to yield ethyl β-diethoxycarbonylmethyl-β-(4-pyridyl)propionate. Reduction of the triester over platinum to the piperidine stage, followed by bromination and cyclisation of the bromoester in boiling pyridine, gave 55% of 3-(ethoxycarbonylmethyl)-2,2-(diethoxycarbonyl)quinuclidine (XLII). When the latter is boiled with hydrochloric acid, 3-carboxymethylquinuclidine-2-carboxylic acid hydrochloride (XLIII) is formed. The ethyl ester of this acid is reduced by lithium aluminium hydride to 3-(β-hydroxyethyl)-2-hydroxymethylquinuclidine which gives 3-(β-chloroethyl)-2-chloromethylquinuclidine with thionyl chloride. The dichloride of 3-carboxymethylquinuclidine-2-carboxylic acid has been converted to several amides which are reduced by lithium aluminium hydride to the amines[31]:



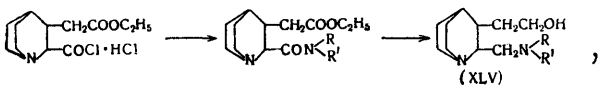
where R = R' = CH_3, C_2H_5; R = H; R' = $C_6H_5CH_2$.

The diethyl ester of 3-carboxymethylquinuclidine-2-carboxylic acid has an interesting property[65]. When its aqueous solutions are kept at room temperature over a long period one of the carbethoxy groups is hydrolysed and an acid ester is formed. Because of the ease of hydrolysis of ethyl quinuclidine-2-carboxylate, this acid ester was considered to be 3-ethoxycarbonylmethylquinuclidine-2-carboxylic acid (XLIV); this structure was confirmed by the conversions mentioned below:



(XLIV)

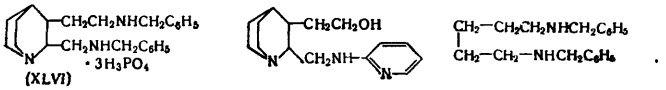
With thionyl chloride the acid ester readily forms an acid chloride which gives amides of 3-ethoxycarbonylmethylquinuclidine-2-carboxylic acid with primary and secondary amines. Reduction of these amides by lithium aluminium hydride yields 3-(β-hydroxyethyl)-2-(alkylaminomethyl)quinuclidines (XLV)[65]:



(XLV)

where R = R' = CH_3, C_2H_5, H; R = H; R' = α-pyridyl; NRR' = 1-piperidyl.

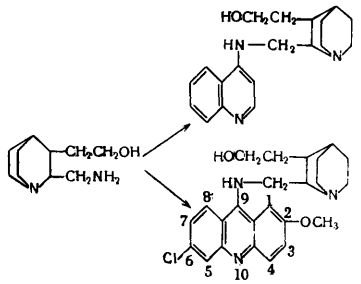
A number of 2,3-disubstituted quinuclidines have ganglion-blocking properties, the highest activity being shown by 2-benzylaminomethyl-3-(β-benzylaminoethyl)quinuclidine triphosphate (XLVI) and 2-(2'-pyridylaminomethyl)-3--(β-hydroxyethyl)quinuclidine[32].



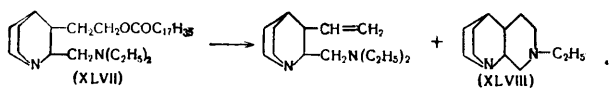
(XLVI)

The latter compound also enhances uterine contractions. It is noteworthy that 1,5-dibenzylaminopentane, which contains an arrangement of atoms incorporated in (XLVI), has no ganglion-blocking properties. This indicates that only a combination of a definite grouping of atoms and the quinuclidine ring gives compounds with a high degree of pharmacological activity.

Compounds (XLV) containing the quinoline or acridine ring system as a substituent on the nitrogen atom were prepared by condensing 2-aminomethyl-3-(β-hydroxyethyl)-quinuclidine with 4-chloroquinoline (in the presence of phenol) and 2-methoxy-6-chloro-9-phenoxyacridine respectively[65].

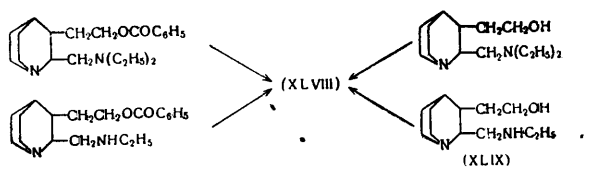


An extensive study has been made of the formation of 2-(N-substituted-aminomethyl)-3-vinylquinuclidines by distilling esters of 2-(N-alkyl- or N,N-dialkyl-aminomethyl)--3-(β-hydroxyethyl)quinuclidines under atmospheric pressure[66]. Two substances are formed from 2-(diethylaminomethyl)-3-(β-stearylhydroxyethyl)quinuclidine (XLVII): 2-diethylaminomethyl-3-vinylquinuclidine and 1'-ethylpiperidino-3',4' : 2,3-quinuclidine (XLVIII), the yield of the former being approximately 10% of the total:

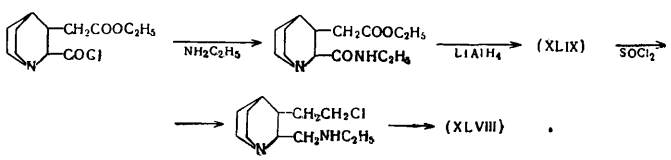


Ethyl stearate was also isolated from the distillation products of (XLVII), thus confirming the formation of the tricyclic compound (XLVIII).

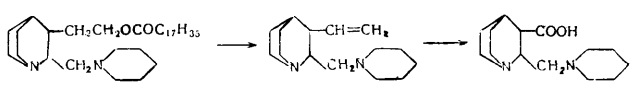
Distillation of 2-diethylaminomethyl- and 2-ethylaminomethyl-3-(β-hydroxyethyl)quinuclidine benzoate, or heating the alcohols with phthalic anhydride in the presence of benzenesulphonic acid, gives only (XLVIII):



The structure of (XLVIII) was confirmed by synthesis as follows:

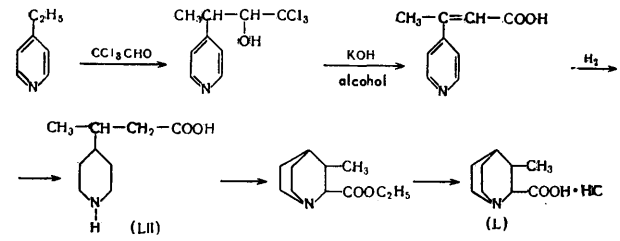


Distillation of 2-(N-piperidinomethyl)-3-(β-stearylhydroxyethyl)quinuclidine at atmospheric pressure yields a single product, namely 2-(N-piperidinomethyl)-3-vinylquinuclidine. The position of the double bond was proved by the oxidation of this compound to 2-(N-piperidinomethyl)-quinuclidine-3-carboxylic acid[66].

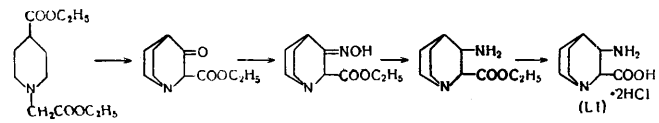


It was shown that distillation of esters of 2-(diethyl- and ethylaminomethyl)-3-(β-hydroxyethyl)quinuclidine gives predominantly the tricyclic compound (XLVIII) formed by simultaneous elimination of a molecule of ester or acid derived from the acyl group esterifying the original alcohol and an alkyl group or hydrogen of the aminomethyl group in the 2-position of the quinuclidine nucleus. Only the vinyl derivative is obtained upon distillation of compounds in which the nitrogen atom in the aminomethyl group forms part of a cyclic system which is stable to fission at high temperature.

3-Methylquinuclidine-2-carboxylic acid (L) and 3-aminoquinuclidine-2-carboxylic acid (LI) are also members of the 2,3-disubstituted series of quinuclidine derivatives. The ethyl ester of the acid (L) was synthesised[67] by successive treatment of β-(4-piperidyl)butyric acid (LII) with phosphorus trichloride, bromine, absolute ethyl alcohol, and pyridine. The procedure may be represented as follows:

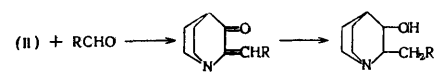


Compound (LI) was prepared as follows[68]:



Dieckmann cyclisation of 1-ethoxycarbonylmethyl-4--ethoxycarbonylpiperidine gives ethyl 3-quinuclidone-2--carboxylate. This forms an oxime which is reduced over platinum to an amino-ester which can be hydrolysed to (LI).

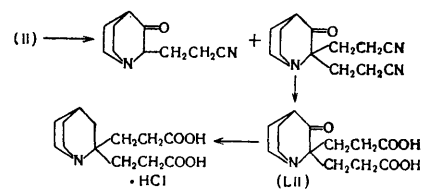
A number of 2,3-disubstituted quinuclidine derivatives have been obtained from 3-quinuclidone. When the ketone is condensed with 4-formylquinoline and benzaldehyde, a substituted ruban[69] and 2-benzal-3-quinuclidone[50] are formed respectively. Reduction of these compounds saturates the double bond and converts the keto-group to hydroxyl.



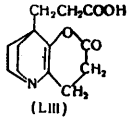
where R = phenyl and 4-quinolyl.

The tropic and diphenylacetic acid esters of 2-benzyl-3--hydroxyquinuclidine were synthesised and found to be pharmacologically inactive[50].

Since 3-quinuclidone contains an active methylene group, it can be condensed with acrylonitrile[36], giving a mixture of 2-(β-cyanoethyl)-3-quinuclidone and 2,2-di(β-cyanoethyl)--3-quinuclidone:



The structure of the former was proved by converting it to β-(2-quinuclidyl)propionic acid (see above), that of the latter by hydrolysis to the keto-diacid (LII). When (LII) was treated with acetic anhydride compound (LIII),



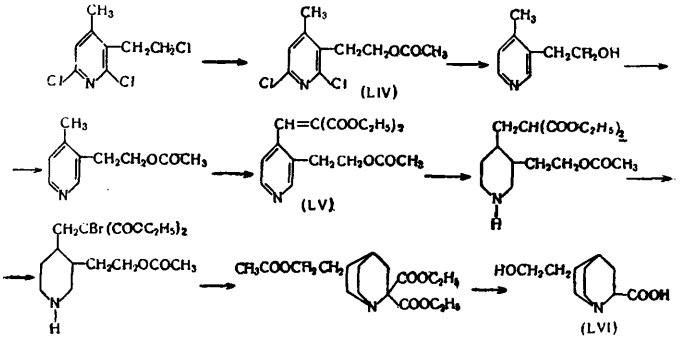
(LIII)

was not formed, demonstrating that the cyanoethyl groups were not in positions 2 and 4. Therefore, the keto-dinitrile was ascribed the structure of 2,2-di-(β-cyanoethyl)--3-quinuclidone. Compound (LII) was converted to a diacid by the Wolf–Kishner reaction.

2,5-Disubstituted Quinuclidines

Little has been published concerning the synthesis of 2,5-disubstituted quinuclidines owing to relative unavailability of 3,4-disubstituted pyridines and of suitable dihalogeno-alkylamines and trihalogeno-alkanes with a branching carbon skeleton.

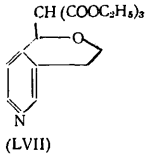
Up to now, apart from quinine alkaloids, their analogues and isomers (to which a special section of the present review is devoted), only 5-(β-hydroxyethyl)quinuclidine-2--carboxylic acid, 5-(β-methoxyethyl)quinuclidine-2-carboxylic acid, 5-quinuclidone-2-carboxylic acid, and some of their derivatives have been synthesised, using a trichloromethylethylpyridine[70,71].



(LIV) (LV) (LVI)

This trichloromethylethylpyridine, treated with potassium acetate in glacial acetic acid at 175°, gives compound (LIV) which, after dehalogenation with hydrogen in the presence of a palladium catalyst and reacetylation, condenses with mesoxalic ester to give 3-(β-acetoxyethyl)-4-(β,β-diethoxycarbonylvinyl)pyridine (LV). Catalytic hydrogenation of (LV) followed by bromination and cyclisation of the product gives 5-(β-acetoxyethyl)-2,2-diethoxycarbonylquinuclidine which, on boiling with concentrated HCl, forms 5-(β-hydroxyethyl)quinuclidine-2-carboxylic acid (LVI).

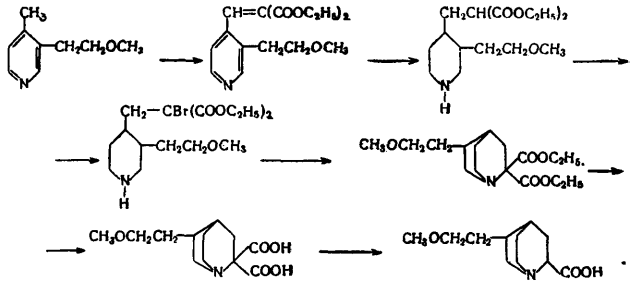
A bicyclic compound, 2-diethoxycarbonylmethylpyridino--3',4':3,4-dihydropyran (LVII), is formed when 3-(β-acetoxyethyl)-4-methylpyridine is condensed with mesoxalic ester. This compound was isolated as the hydrochloride in 11% yield; the yield of 3-(β-acetoxyethyl)-4-(β,β-diethoxycarbonylvinyl)pyridine was 36%.



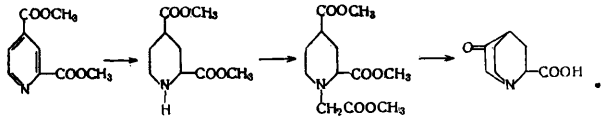
(LVII)

The authors explain the formation of compound (LVII) by the mobility of the acetoxyl group.

In order to improve the yield of the substituted diethoxycarbonylvinylpyridine, mesoxalic ester was condensed with 3-(β-methoxyethyl)-4-methylpyridine[72] to prepare 5-(β--methoxyethyl)quinuclidine-2-carboxylic acid by a route similar to that used for the preparation of compound (LVI)[73].



5-Quinuclidone-2-carboxylic acid and some of its derivatives have been prepared using the lutidine fraction of pyridine bases as starting material[68].

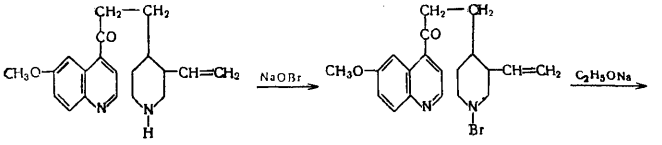


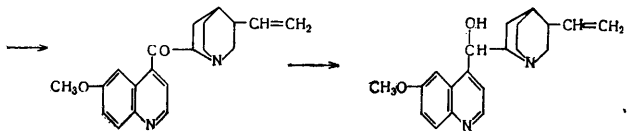
Dimethyl pyridine-2,4-dicarboxylate, obtained from 2,4--lutidine, is hydrogenated over platinum to the corresponding piperidine. This is then alkylated on the nitrogen with bromacetic ester and the product is cyclised by the Dieckmann method to 5-quinuclidone-2-carboxylic acid. The methyl and diethylaminoethyl esters of this acid, as well as the methyl esters of 5-hydroxy- and 5-acetoxyquinuclidine-2-carboxylic acid, have been described.

SYNTHESIS OF QUININE ALKALOIDS, THEIR ANALOGUES, AND ISOMERS

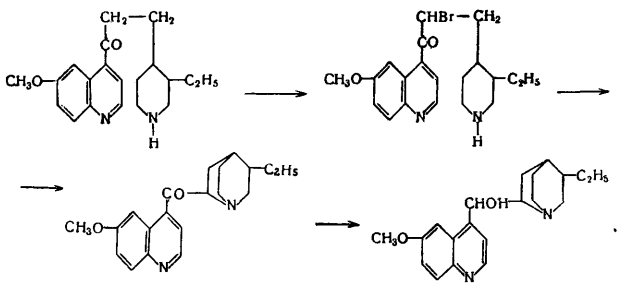
Until the last decade all research into the synthesis of quinuclidine derivatives had been directed towards methods of preparation of quinine alkaloids and their analogues and isomers. Detailed reviews of the quinine alkaloids have been published[74-76] concerning the history of their discovery and application, natural occurrence, analytical methods, isolation from cinchona bark, and investigation of structure, conversions, and stereochemistry. The present review is therefore limited to the synthesis of those quinine alkaloids and their analogues and isomers which are derived from quinuclidine.

The synthesis of quinine was attempted long before, but systematic studies only became possible after the elucidation of the structural formula of quinine alkaloids in 1908[77]. Rabe laid the foundation for these studies when he showed that quinotoxine (a fission product of natural quinine with the quinuclidine ring opened[78]) could be converted to quinine[79] as follows:



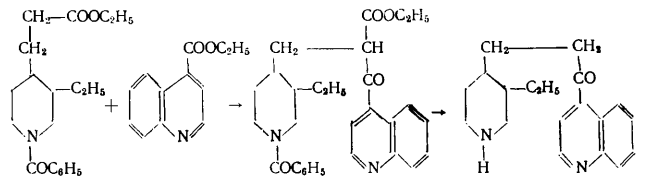


The similar conversion of hydroquinotoxine to hydroquinine gives better yields[80]. The former is brominated to give a C-bromo derivative which is cyclised to hydroquininone. The ketone is reduced catalytically, giving a mixture of stereoisomeric carbinols from which hydroquinine and hydroquinidine are isolated:



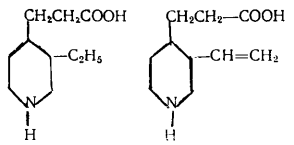
This progress in the partial syntheses of quinine and hydroquinine reduced the problem of synthesis of quinine alkaloids to the preparation of the appropriate toxines.

Rabe[81] showed that hydrocinchotoxine (LVIII) could be obtained by Claisen condensation of ethyl cinchoninate and ethyl ester of N-benzoylhomocincholoipon followed by hydrolysis and decarboxylation of the product.



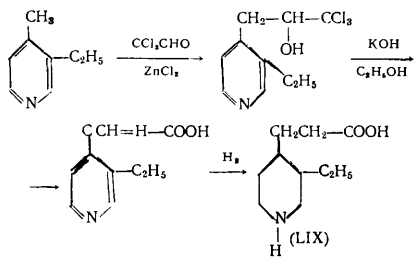
(LVIII)

The most difficult part of this synthesis is the preparation of the substituted ethyl β-(N-benzoyl-4-piperidyl)propionates: homocincholoipon (LIX) and homomeroquinene (LX)



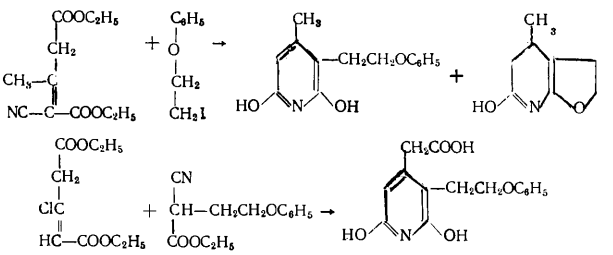
(LIX) (LX)

3-Ethyl-4-methylpyridine was used as the starting material for the synthesis of *d,l*-homocincholoipon (LIX) by Koenigs and Ottmann[82] by the route



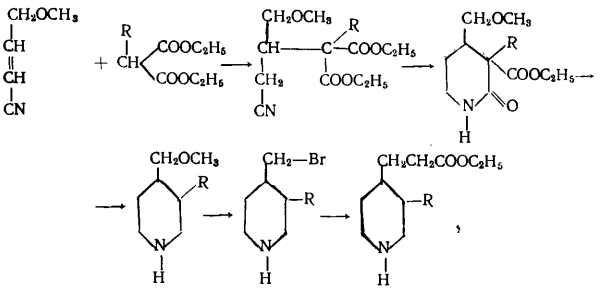
Rabe et al.[83] developed this synthesis and described the separation of ethyl ester of *d,l*-homocincholoipon into its optically active components. These studies led to the complete synthesis of the dihydro bases of some quinine alkaloids including hydroquinine and hydroquinidine.

In the synthesis of β-(3-vinyl-4-piperidyl)propionic acid (LX) the greatest difficulties were associated with the formation of the vinyl group. Matejka, Robinson, and Watt[84] were the first in this field; they condensed ethyl α-cyano-β-methylglutaconate with β-phenoxyethyl iodide and obtained 2,6-dihydroxy-3-(β-phenoxyethyl)-4-methylpyridine and 4-methyl-6-hydroxydihydrofurano-2',3' : 2,3-pyridine. They also prepared 2,6-dihydroxy-3-(β-phenoxyethyl)-4-(carboxymethyl)pyridine by condensing ethyl α-cyano-γ-phenoxybutyrate and ethyl β-chloroglutaconate:



Attempts to reduce these 2,6-dihydroxy pyridines and 6-hydroxydihydrofurano-2',3' : 2,3-pyridine to the corresponding piperidines were unsuccessful. Homomeroquinene could not be obtained from 4-methylfurano-2',3' : 2,3-pyridine since the latter's γ-methyl group does not condense with chloral[85].

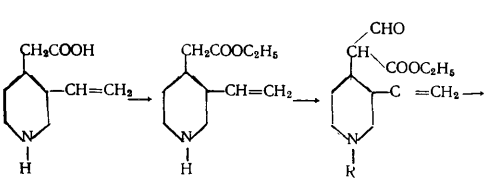
Koelsch et al. made an extensive study of methods of preparation of homomeroquinene and showed that hydrogenation of certain substituted γ-cyanobutyric esters is accompanied by cyclisation to esters of substituted 2-piperidone-3- or -5-carboxylic acids. The latter may be reduced by sodium in butanol to the corresponding piperidines. Koelsch[86,87] used these reactions for the synthesis of ethyl β-(4-piperidyl)propionate and a number of esters of 3-substituted β-(4-piperidyl)propionic acids:

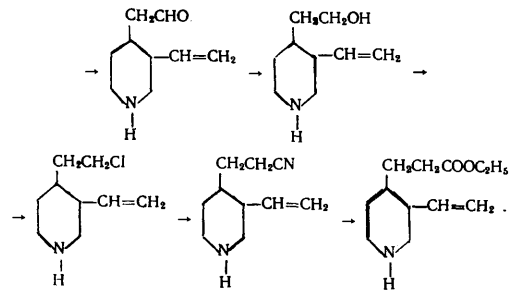


where R = H, C_2H_5, $CH_2CH_2OCH_3$, $CH_2CH_2OC_2H_5$.

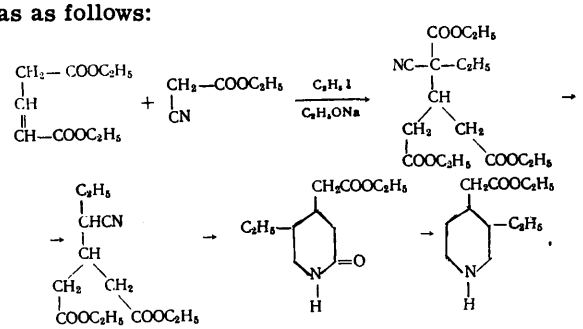
Analogues of quinine alkaloids can be prepared from these compounds in the usual way. However, further work in this field was interrupted by the Second World War.

Livshits, Preobrazhenskii, and Baryshnikova[88] proposed a method of preparation of homomeroquinene starting from meroquinene:

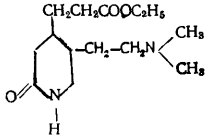




Several stages of the proposed synthesis were carried out. In 1951 Preobrazhenskii, Evstigneeva, et al.[89] suggested routes for the preparation of cincholoipon, meroquinene, and homomeroquinene which were considerably different to those of Koelsch. The suggested scheme for cincholoipon was as follows:

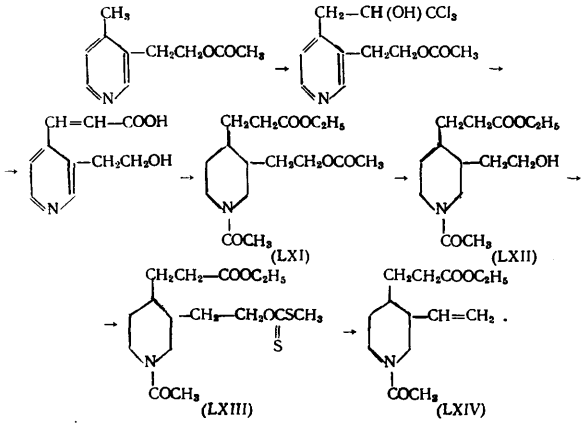


By using a β-dimethylaminoethyl halide instead of ethyl iodide these workers obtained 5-(β-dimethylaminoethyl)-4-(β-ethoxycarbonylethyl)-2-piperidone,



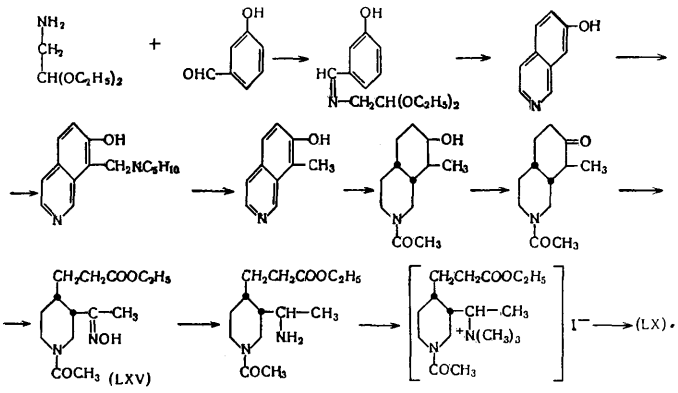
and suggested that this compound could be converted into meroquinene. A similar scheme, starting with diethyl dihydromuconate, was proposed for the synthesis of homomeroquinene. In 1958 the same workers[89] successfully synthesised cis-trans-homocincholoipon from cincholoipon via the alcohol, chloride, and cyanide.

Racemic homomeroquinene was synthesised using a trichlorocollidine (trichloro-3-ethyl-4-methylpyridine) as starting material[90]:



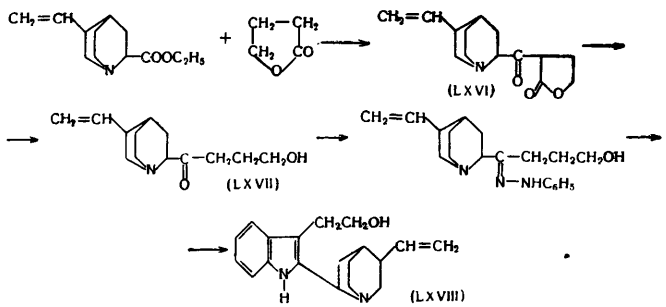
3-(β-Acetoxyethyl)-4-methylpyridine, obtained from the trichlorocollidine (see above), condenses with chloral. Hydrolysis of the product gives β-(3-hydroxyethyl-4-pyridyl)-acrylic acid which is converted by successive esterification, hydrogenation, and acetylation into 1-acetyl-3-(β-acetoxyethyl)-4-(β-ethoxycarbonylethyl)piperidine (LXI). Studies showed that under certain conditions the *O*-acetyl group could be split off selectively, with preservation of the *N*-acetyl residue, by alcoholysis of (LXI) with alcoholic hydrogen chloride. Various methods for converting the 3-(β-hydroxyethyl) group in compound (LXII) into a vinyl group were investigated: dehydration with concentrated sulphuric acid or phosphorus pentoxide, its conversion into a β-halogoethyl group with subsequent treatment with alcoholic potash, and preparation of 1-acetyl-4-(β-ethoxycarbonylethyl)-3-(β-dimethylaminoethyl)piperidine methiodide followed by Hoffman fission. These studies demonstrated that racemic *N*-acetylhomomeroquinene (LXIV) could only be obtained in small yield when methyl β-[4-(β-ethoxycarbonylethyl)-1-acetyl-3-piperidyl]ethylxanthate (LXIII) was decomposed thermally.

dl-cis-Homomeroquinene was prepared by Woodward and Doering[91] who were the first to achieve a complete synthesis of quinine:



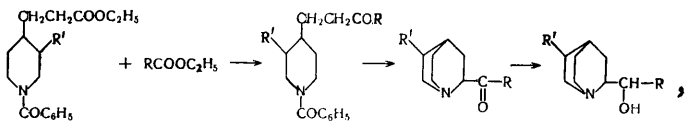
7-Hydroxyisoquinoline, obtained by the Fritsch method from *m*-hydroxybenzaldehyde and aminoacetaldehyde acetal via the Schiff's base, served as starting material. This condenses with formaldehyde and piperidine in methanol solution to 7-hydroxy-8-piperidinomethylisoquinoline which on heating to 220° with sodium methoxide yields 7-hydroxy-8-methylisoquinoline. The latter is reduced stepwise, first to the tetrahydroisoquinoline, and then (after acetylation) to a mixture of stereoisomeric 2-acetyl-7-keto-8-methyldecahydroisoquinolines from which the cis-isomer is isolated. When the latter is treated with ethyl nitrite in the presence of sodium ethoxide, the ester (LXV) is obtained, which on subsequent reduction, exhaustive methylation, and Hoffman fission, gives homomeroquinene (LX). This is converted to quinine by Rabe's method. Separation of the optically active isomers was achieved using the dibenzoyltartrates at the quinotoxine stage. This complete synthesis of quinine, achieved in 1944, was an important milestone in the chemistry of quinuclidine derivatives.

Chen' Chan-bai, Evstigneeva, and Preobrazhenskii[92] carried out a partial synthesis of cinchonamine — a quinine alkaloid containing a quinuclidine and an indole nucleus — starting from ethyl 5-vinylquinuclidine-2-carboxylate:



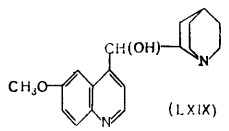
The acid had been prepared earlier by oxidation of naturally occurring quinamine[93]; the ethyl ester condenses with γ-butyrolactone to give the compound (LXVI). When the latter is heated with sulphuric acid, the lactone ring opens and the product undergoes decarboxylation to form (LXVII), the phenylhydrazone of which was converted by a modified Fischer reaction into cinchonamine (LXVIII), identical with the natural alkaloid.

Some syntheses of quinine alkaloid analogues and isomers, based chiefly on Rabe's scheme, consisted of condensation of esters of β-(1-benzoyl-4-piperidyl)propionic acid, or its derivatives, with an acid, followed by closure of the quinuclidine ring and reduction of the ketone thus formed to a corresponding substituted quinuclidine-2-carbinol:

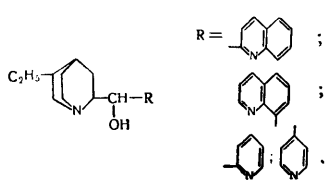


where R' = H, C_2H_5.

This method was used for the synthesis of 6-methoxy-9--rubanol (LXIX)[94,95], which differs from quinine in the absence of a vinyl group on the quinuclidine nucleus. Two stereoisomers of this compound (which correspond in configuration to quinine and quinidine) and their racemate proved very close to quinine in their anti-malarial activity:

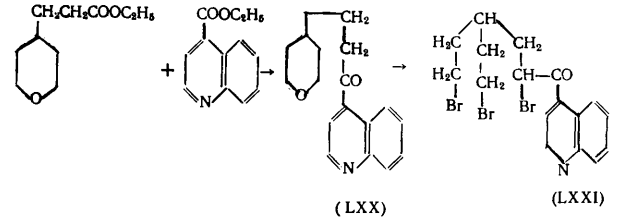


A similar route was used in the preparation of the following compounds. (5-Ethyl-2-quinuclidyl)(6'-methoxy-8'--quinolyl)carbinol[96] and (5-ethyl-2-quinuclidyl)(6'-methoxy--2'-quinolyl)carbinol[97] are isomers of hydroquinine with a quinuclidylhydroxymethyl group in the 2- and 8-positions of the quinoline nucleus. (5-Ethyl-2-quinuclidyl)(4'-pyridyl)-carbinol[98] and (5-ethyl-2-quinuclidyl)(2'-pyridyl)carbinol[99] are analogues of hydrocinchonine, containing a 2- or 4-substituted pyridine ring instead of the quinoline nucleus. (2-Quinuclidyl)(4'-pyridyl)carbinol[100], (2-quinuclidyl)(2'--pyridyl)carbinol[101] and (2-quinuclidyl)(1'-naphthyl)carbinol[102] and isoquinoline analogues of quinine alkaloids (as the ketones)[103] were also prepared.

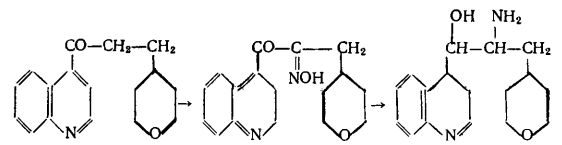


Chemotherapeutic investigations revealed that substitution of a 4-pyridyl ring for the quinoline nucleus in hydroquinine gives a compound which retains the antimalarial properties of hydroquinine.

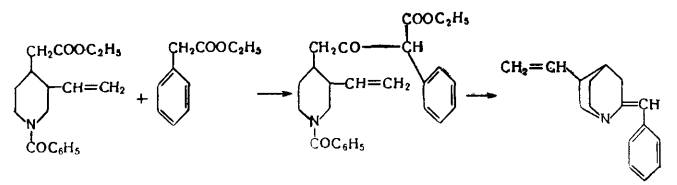
Prelog attempted to obtain quinine alkaloid analogues from compounds of the tetrahydropyran series[104] by a method similar in principle to that of Rabe:



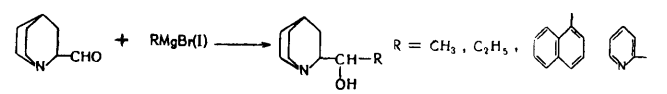
Ethyl cinchoninate was condensed with 4-(β-ethoxycarbonylethyl)tetrahydropyran and the condensation product (LXX) was converted to the tribromide (LXXI) by fuming hydrobromic acid, but attempted cyclisation of (LXXI) failed. (4'-Quinolyl)(2-quinuclidyl)carbinol was not obtained by "double intramolecular alkylation" of the amino alcohol synthesised as follows:



Kenner and Nandi[105] made use of Rabe's scheme for the preparation of 2-benzylidene-5-vinylquinuclidine, an analogue of dehydrated quinine alkaloids, from ethyl esters of N-benzoylmeroquinene and ethyl phenylacetate:



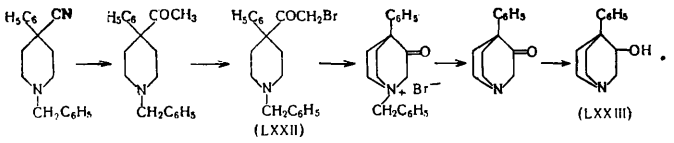
Recently a new method has been described for the synthesis of substituted quinuclidine-2-carbinols[106], based on the reaction between 2-formylquinuclidine with Grignard reagents:



This method has been used for the preparation of the following compounds: (2-quinuclidyl)methylcarbinol, (2-quinuclidyl)ethylcarbinol, (2-quinuclidyl)(1'-naphthyl)carbinol and (2-quinuclidyl)(2'-pyridyl)carbinol. (2-Quinuclidyl)-methylcarbinol has also been prepared by catalytic reduction of 2-acetylquinuclidine (synthesis described above) in the presence of platinum. Both this reduction in an alcoholic medium and the method employing Grignard reagents give a mixture of diastereoisomeric (2-quinuclidyl)methylcarbinols. By reduction in an aqueous medium, only one diastereoisomer of this compound was obtained.

3,4-Disubstituted Quinuclidines

Only one report has been published[107] on the synthesis of 3,4-disubstituted quinuclidines. It described the synthesis of 4-phenyl-3-hydroxyquinuclidine:



1-Benzyl-4-phenyl-4-cyanopiperidine reacts with lithium methyl to form 1-benzyl-4-phenyl-4-acetylpiperidine which is converted to the bromide (LXXII) by bromine in glacial acetic acid. The bromide cyclises to 1-benzyl-4-phenyl--3-ketoquinuclidinium bromide. By eliminating benzyl bromide and reducing the product with lithium aluminium hydride, 4-phenyl-3-hydroxyquinuclidine (LXXIII) is obtained. The alcohol (LXXIII) was esterified with acetic and propionic anhydrides but the esters obtained showed no analgesic properties.

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REFRACTOMETRY AS A METHOD FOR THE PHYSICOCHEMICAL ANALYSIS OF ORGANIC SYSTEMS

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INTRODUCTION

Refractometry was the first optical method to be applied in chemistry and it has been widely used for structure determination, identification, and quantitative analysis. Less attention has been paid to the possibility of using refractometry for physicochemical analysis, i.e. to gain information about the interaction between the components of chemical systems and on their association or dissociation, from the shape of the refractive index vs. composition curves.

The organic chemist faced with the necessity of studying the nature of liquid systems in connection with problems of molecular-compound formation and the mechanism of organic reactions finds the universal, readily available, and simple refractometric method extremely attractive. The present article describes critically the basis of the refractometric method of physicochemical analysis and the history of its application to organic systems, and examines the possibility of further applications. A critical analysis is also of interest in connection with the study of the methodology of physicochemical analysis as developed by N. S. Kurnakov (1860–1941) and his school. In the works of Anosov, Pushin, and Trifonov, we find the statement and interpretation of the relationships between the shapes of property vs. composition diagrams and the physicochemical processes in the systems studied, in terms typical of Kurnakov's methodology. The study of this methodology extends beyond the refractometric method, and is of interest in relation to the critical evaluation of analogous methods based on the measurement of other properties, such as dielectric constant, surface tension, viscosity, etc.

In the present paper we shall restrict ourselves to binary systems, but the principal features established for binary systems also hold for ternary systems.

I. ORIGINS OF THE REFRACTOMETRIC METHOD OF PHYSICOCHEMICAL ANALYSIS AND ITS DEVELOPMENT IN THE FIRST HALF OF THE 20TH CENTURY

The possibility of using refractometry for the study of compounds formed in solution appears to have been first indicated in a paper by Deville[1], who detected refractive-index maxima in aqueous solutions of acetic acid and methyl and ethyl alcohols. Deville noted that the position of the maxima corresponded closely to integral molar ratios of the components, and expressed the hope that the singular points on the refractive-index curves might be used to study compounds in solution. This idea, however, was not developed until 50 years later.

Fery[2] found that the equivalence points in neutralisation reactions corresponded to angular points on the refractive-

-index isotherms of the mixed solutions. In such systems, according to Fery, the refractive-index curves consist of intersecting straight lines.

Almost simultaneously, the effect of double-decomposition reactions in salt solutions on the values of the refractive index was examined by Verschaffelt[3], who studied mixtures of solutions having almost identical refractive indices. With this choice of concentrations of the solutions to be mixed, deviations from additivity led to the appearance of maximum and minimum refractive-index values. From a survey of the conditions under which these values were obtained, Verschaffelt concluded that in mixed electrolyte solutions, negative deviations from additivity characterised chemical interaction between the components, while positive deviations indicated chemical interaction only when they could not be attributed to contraction, since maximum values of n were observed when very concentrated solutions of salts with identical refractive index were mixed, even when no reaction took place between the dissolved salts.

Verschaffelt also detected refractive-index maxima in mixtures of water with butyric and valeric acids, and noted that the maxima were displaced to higher concentrations of acid with increase in the molecular weight of the latter[4]. Refractive-index maxima were also observed in mixtures of carboxylic acids and alcohols (of similar structure), but these did not correspond to equimolar compositions. One of the first successful attempts to use refractometry to detect unstable organic compounds was made in an investigation of the acetaldehyde–ethyl alcohol system[5]. A clearly defined maximum value of n_D^{18} was observed at an equimolar component ratio, indicating hemiacetal formation.

In addition to the study of refractive-index curves, attempts were made at the start of the 20th century to find the relationship between the deviations of molecular refractions from additivity and the non-ideal nature of binary systems, particularly as revealed by deviations from Raoult's law. In azeotropic systems, however, additivity of molecular refraction was observed, except in a few cases[6]. Similarly, no direct relationship could be found between the sign of the deviation from additivity of the molecular refractions and vapour pressures[7].

At the end of the 19th and start of the 20th centuries, an attempt was made to use refractometry to confirm Mendeleev's hydrate theory of solutions and to establish the effect of electrolyte dissociation on the refractive properties (by Pickering, Jones, Leblanc, Walden, and others), but a discussion of this work is beyond the scope of the present article. In a review of the above early works on the refractometric study of solutions, Kremann[8] pointed out that deviations of the refractive properties from additivity are possible, but not essential, features of association and dissociation processes. On the other hand, deviations from a linear relationship are observed even in the absence of interaction, so that the study of the refraction of light, in Kremann's opinion was "little suited to the examination of the constitution of binary liquid mixtures".

The subsequent development of the refractometric method of physicochemical analysis was closely related to the work of Kurnakov and his school. From 1908–1909 onwards, they undertook an extensive study of organic systems by the various methods of physicochemical analysis, and Glazunov, a graduate of the Polytechnic Institute, undertook the study of the refractive index vs. composition diagrams[9].

Glazunov studied 9 binary organic systems, classifying them into three groups according to the nature of the interaction between the components:

Group 1. The refractive index is a linear function of the composition (in mole fractions) — systems where no chemical interaction takes place (benzene–aniline, chloroform–bromoform, etc.).

Group 2. The refractive-index diagram consists of two straight lines intersecting at a point corresponding to a non-dissociated compound — "rational" systems (Kurnakov's terminology) such as mustard oils–secondary amines.

Group 3. Curves are obtained (sometimes with a maximum) — "irrational" systems in which unstable dissociated compounds are formed (acetone–water, acetic acid–aniline, etc.).

Glazunov's classification of refractive index diagrams was based on a limited number of not very accurate data. The problem of the relationship between the shape of the refractive-index curves and the nature of binary systems was examined much more thoroughly by Anosov[10–12]. Like Glazunov, he considered it necessary to construct the refractive-index diagrams using mole percentages to express the composition. From a study of 15 systems and the literature data for approximately 50 more, Anosov modified Glazunov's classification as follows:

1) The branches of the diagrams with singular points should in general be curves, and not straight lines.

2) The isotherms of the third group are characterised not by general curves, but by curves convex away from the concentration axis.

3) A further group of isotherms must be introduced — — those convex towards the axis of abscissae and characteristic of systems with a component which dissociates on dissolution in the other.

Thus according to Anosov there existed four classes of refractive-index isotherm, each of which reflected a definite type of interaction between the components in binary systems.

1) Straight lines, or lines with very small curvature, usually convex towards the composition axis — ideal or almost ideal (normal) systems.

2) Curves with a marked convexity towards the composition axis — systems in which one component dissociates on dissolution in the other.

3) Curves with a marked convexity away from the composition axis (sometimes with a maximum) — "irrational" systems, where a more or less extensively dissociated compound is formed.

4) Curves with a singular point, consisting of two intersecting branches and observed only in rational systems where an undissociated compound is formed.

Anosov's classification was completely analogous to that of other composition vs. property diagrams, developed by Kurnakov's school, and appeared in basic text-books on physicochemical analysis[13,14].

The principles upon which Anosov based his interpretation of the shape of the non-singular refractive-index isotherms may be formulated as follows:

1) In ideal systems the refractive index is an additive function of the mole fractions of the components:

$$n = n_1N_1 + n_2N_2 \qquad (1.1)$$

where n_1 and n_2 are the refractive indices of the components

and N_1 and N_2 are their mole fractions.

2) The nature of the chemical processes taking place in the system determines uniquely whether the $n(N)$ isotherms are convex or concave towards the x-axis*. The formation of compounds leads to *positive* deviations from additivity $\Delta n(N)$:

$$\Delta n(N) = n_{exp} - n_1N_1 - n_2N_2, \quad (1.2)$$

and dissociation of associated components leads to the opposite effect — *negative* deviations $\Delta n(N)$.

During the nineteen-thirties and -forties, the great majority of papers on the application of refractometry to the study of organic systems was based on these principles and on the corresponding classification of refractive-index curves. Particular mention must be made of the extensive studies carried out by the noted Russian chemist Pushin and his school at Belgrade University[15-45]. The refractometric method was also used for the study of organic systems by Trifonov and his school[46-55] and others[56-66].

The above principles are apparently completely logical. However, attempts to apply the classification in practice have led to numerous difficulties and contradictions.

By attributing significance even to small deviations from additivity $\Delta n(N)$ of the order of $1-2\times10^{-3}$, Anosov concluded that the positive values of $\Delta n(N)$ in the dimethylaniline–allyl isothiocyanate system indicated "some chemical interaction"[10,12]. This conclusion contradicts the well-known fact that tertiary amines do not react with isothiocyanates, and is not in accordance with viscosimetric data. Anosov tried to explain these and certain other analogous cases of non-correspondence between the refractive-index curves and other properties by postulating, for almost all substances, a certain tendency to undergo chemical interaction and also to undergo association[12-14]. "If one of these tendencies is marked, then it appears on the isotherms for all the properties, and suppresses the other. For systems close to ideal, however, neither tendency predominates, although it is possible that the isotherms for different properties have different sensitivity towards these tendencies...."[12].

This interpretation, although it may be applicable to normal systems, is not applicable to those showing considerable deviations from ideal behaviour. At the same time, non-correspondence between refractometric and other properties has for long been known even in typical irrational systems.

Ust'-Kachkintsev[65] studied the ethylene diamine–water system and pointed out that refractometry indicates only the existence of the dihydrate $C_2H_4(NH_2)_2 \cdot 2H_2O$. The formation of the stable monohydrate, whose existence in the liquid phase is undisputed, cannot be detected.

A number of very strange cases of non-correspondence between the shape of the refractive-index curves and the diagrams typical of irrational systems was observed by Matavul'[30,32]. In mixtures of quinoline and pyridine with higher fatty acids — oenanthic, caprylic, pelargonic and capric — *negative* deviations from additivity $\Delta n(N)$ were observed and the $n(N)$ curves had the shape typical of systems with non-interacting associated components, although in these systems acid-base interaction undoubtedly takes place. At the same time, mixtures of lower carboxylic acids with the same bases showed positive deviations $\Delta n(N)$ (Fig. 1). This curious change in the sign of the $n(N)$ isotherms on going from the lower members of the homologous series to the higher could not then be satisfactorily explained*. Despite the convictions of Anosov[13,14], who did not know of this work, the existence of negative $n(N)$ isotherms in irrational systems showed that class 2 of his classification was not distinct.

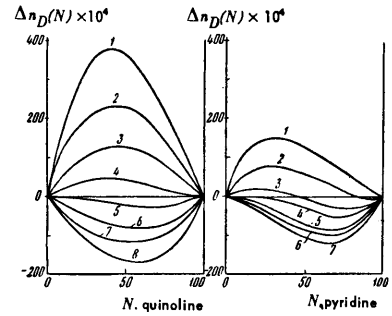


Fig. 1. Deviations of the refractive index from additivity, $\Delta n(N)$, in mixtures of quinoline and pyridine with carboxylic acids: 1) propionic; 2) butyric; 3) valeric; 4) caproic; 5) oenanthic; 6) caprylic; 7) pelargonic; 8) capric.

In connection with the difficulties encountered in the refractometric study of irrational systems, mention must be made of the work of Usanovich and Stepan'yants[66]. In the arsenic trichloride–diethyl ether system, where electrical conductivity and viscosity data show that a compound of equimolecular composition is formed, these authors found an almost linear $n(N)$ isotherm, which, according to Glazunov, Anosov, and Pushin, was characteristic of ideal systems. This contradiction led Usanovich and Stepan'yants to doubt the accuracy of formula (1.1) for refractive-index additivity. Referring to an early paper by Pulfrich[67] on the relationship between refractive index and the density of solutions, they pointed out that in ideal systems the refractive indices should be additive as functions of the component concentrations expressed in *volume* fractions:

$$n = n_1V_1 + n_2V_2. \quad (1.3)$$

When this is done, positive deviations from additivity are obtained in the $AsCl_3$–$(C_2H_5)_2O$ system

$$\Delta n(V) = n_{exp} - n_1V_1 - n_2V_2, \quad (1.4)$$

and the disagreement with data obtained by other methods disappears.

* The symbol $n(N)$ denotes the refractive index n, regarded as a function of the composition expressed as the mole fraction N. The functional dependence of n on composition in volume V and weight P fractions will be denoted by $n(V)$ and $n(P)$ respectively.

* Matavul' tried (on insufficient factual grounds) to ascribe it to "the influence of association of the acids"[30, 30,32].

In work on the refractometric method of physicochemical analysis, uncertainty in the formulation of the additivity rule existed long before 1940 and has continued until very recent times. The formulation (1.3) was used by Verschaffelt[3], and the necessity of using this form was confirmed by Mac-Farlane and Wright[68], but their views were completely ignored in work on physicochemical analysis. Until 1947, Trifonov and his school used rule (1.1) exclusively[46-48], but since then they have considered the $n(V)$ curves *together with* the $n(N)$ curves[49-52], with the statement that in a number of cases the former are more demonstrative[51]. Trifonov and his school, however, have not attributed fundamental significance to this formulation of the additivity rule, and have occasionally used mole fractions alone[53-55]. Certain workers[69], moreover, have constructed refractive-index diagrams with composition expressed in *weight* fractions (or percentages), formulating the additivity rule in the form

$$n = n_1P_1 + n_2P_2, \tag{1.5}$$

and regarding the deviations from additivity as

$$\Delta n(P) = n_{exp} - n_1P_1 - n_2P_2. \tag{1.6}$$

From the point of view of scientific logic, it is curious that Pushin, who in his first works[15,16] considered $\Delta n(N)$, in his third paper[17] changed, without comment, to the construction of the $n(P)$ diagrams and the interpretation of the deviations from additivity $\Delta n(P)$. In the many subsequent papers from the Belgrade school[18,20-28,30-40], the $n(N)$ diagrams were again used, and only occasionally the quantities $n(P)$, together with $n(N)$.[19,29] Without being able to explain the non-correspondence between the shape of the $n(N)$ curves and the chemical character of the systems studied, Pushin in such cases simply changed the abscissae of the refractive-index diagrams in such a way as to give the curve the desired shape, agreeing with other data on the behaviour of the components.

Analogous difficulties were encountered by English workers[56]: in the typical eutectic system acetic acid—chlorobenzene, very *pronounced positive* deviations from additivity $\Delta n(N)$ were observed, which were several times greater than the values of $\Delta n(N)$ for the irrational *p*-toluidine–*o*-chlorophenol and *p*-toluidine–*p*-chlorophenol systems.

In 1939 Trifonov and Aleksandrov[46] made an extensive examination of their own and literature data and showed that positive deviations $\Delta n(N)$ were extremely common in systems formed by non-interacting associated components. They pointed out the existence of more than 40 systems of this type, with $n(N)$ curves concave towards the composition axis, instead of convex, as required by Anosov's classification. Anosov[13,14] admitted the indefinite character of the 3rd group of his classification and the impossibility of distinguishing systems formed by non-interacting associated components with positive $\Delta n(N)$ from typical irrational systems, from the shape of the $n(N)$ isotherms. It was still not clear which systems with associated components gave positive values of $\Delta n(N)$ and which gave negative deviations. Trifonov and Aleksandrov[46] postulated the existence of two types of association by molecules of the components. Others[63,70] tried to relate a positive sign for $\Delta n(N)$ to contraction on mixing the components, but it will be seen in Section III that this interpretation is incorrect.

The history of the application of refractometry to the study of the behaviour of components in organic systems reveals a great deal of inexplicable contradictions, which must be regarded as a result of the purely empirical approach to the problem and neglect of the theory of specific and molecular refractions. Study of the works cited shows that it is necessary to re-examine the fundamental postulates of the refractometric method of physicochemical analysis and to put it on a more rigorous basis. The subsequent sections give the results of investigations with this objective, carried out since 1951.[71-79]

II. THE ADDITIVITY OF REFRACTIVE INDICES

The above review of the literature shows that conclusions about the nature of the interaction between the components of organic systems from the shape of the refractive-index curves were most frequently based on the direction of the convexity of the curves, i.e. on the *sign of the deviations from additivity*. In the great majority of papers[9-16,18-28,30-40,46-65] and text books[13,14], the additivity of $n(N)$ (1.1) was assumed, the additivity of $n(V)$ (1.3) and $n(P)$ (1.5) being assumed only in a few cases. In all these papers, no great significance was attached to the foundations of the additivity rule, and no particular attention was paid to it, although the formulation of the rule is of fundamental importance to any conclusions based on deviations from additivity.

Let us examine this problem from the point of view of specific-refraction theory. Many formulae have been proposed for the specific refraction r, and these may all be written in the general form

$$r = \frac{f(n)}{d}, \tag{2.1}$$

where d is the density of the substance and $f(n)$ is a function of the refractive index, the form of which depends on the particular physical theories of optical refraction and on the magnitude of the internal electric field in the dielectric, acting on a molecule surrounded by polarised molecules.

Examples of the more familiar functions $f(n)$ are:

$$f(n) = n - 1 \quad \text{(Gladstone–Dale)}, \tag{2.2}$$

$$f(n) = n^2 - 1 \quad \text{(Newton–Laplace)}, \tag{2.3}$$

$$f(n) = \frac{n^2-1}{n^2+2} \quad \text{(Lorentz and Lorenz)}, \tag{2.4}$$

$$f(n) = \frac{(n^2-1)[2n^2+1+2\alpha(n^2-1)/a^3]}{n^2}, \tag{2.5}$$

where α is the polarisability of the molecule and a its radius (Böttcher's formula).

The last of these formulae contains the characteristic molecular parameters α and a, which indicates that there is no absolute rigorous, universal expression for the specific refraction, independent of the nature of the substance in question.

The rule for specific-refraction additivity in binary systems in its general form, may be written

$$r = r_1P_1 + r_2P_2 \tag{2.6}$$

or

$$\frac{f(n)}{d} = \frac{f(n_1)}{d_1}P_1 + \frac{f(n_2)}{d_2}P_2 \tag{2.7}$$

From this it follows that

$$f(n) = f(n_1)V_1 + f(n_2)V_2, \tag{2.8}$$

where $V_1 = \frac{dP_1}{d_1}$ and $V_2 = \frac{dP_2}{d_2}$ are the volume fractions of the components of the mixture. Thus this function should be

additive when the *volume* fractions are used, *irrespective* of the choice of function $f(n)$.

According to modern views [80], universal functions $f(n)$ can correspond only approximately to the additivity condition (2.8), even though the degree of accuracy is very high. According to experimental data obtained towards the end of last century and still valid today [81,82], the Gladstone–Dale formula (2.2) corresponds to the additivity condition (2.8) better than formulae (2.3) and (2.4). Thus when $f(n) = n-1$ and $V_1 + V_2 = 1$ (ideal systems with no volume change), the additivity rule (2.8) becomes

$$n = n_1V_1 + n_2V_2 . \qquad (2.9)$$

Thus the refractive indices of ideal systems are additive functions of volume fractions. Although the Gladstone–Dale formula reproduces experimental data for liquid systems slightly better than the other refraction formulae, it is still not completely rigorous and universal, and the statement that $n(V)$ is additive in ideal systems cannot be regarded as completely rigorous. This feature must be taken into account, although it becomes important only for the interpretation of fairly small deviations from additivity $\Delta n(V)$.

The additivity rules (1.1) and (1.5), which figure in the great majority of papers on refractivity in organic systems, are thus seen to contradict specific-refraction theory. The question then arises of whether this contradiction is real in practice as well as in principle.

There is an absolutely rigorous and universal relationship between the deviations from additivity $\Delta n(N)$, $\Delta n(V)$, and $\Delta n(P)$, (1.2), (1.4), and (1.6)

$$\Delta n(N) = \Delta n(V) + (n_1 - n_2)(V_1 - N_1) , \qquad (2.10)$$

and

$$\Delta n(P) = \Delta n(V) + (n_1 - n_2)(V_1 - P_1)^* , \qquad (2.11)$$

so that the relationship between the various formulations of the deviations from additivity is determined by the magnitude of the terms $(n_1-n_2)(V_1-N_1)$ and $(n_1-n_2)(V_1-P_1)$ on the one hand, and the magnitude of $\Delta n(V)$ on the other. The differences between the formulations of the additivity rules (1.1), (1.3), and (1.5) may be neglected when

$$|(n_1 - n_2)(V_1 - N_1)| \ll |\Delta n(V)| , \qquad (2.12)$$

or

$$|(n_1 - n_2)(V_1 - P_1)| \ll |\Delta n(V)| . \qquad (2.13)$$

As a rule, these conditions are not fulfilled. The deviations from additivity $\Delta n(V)$ are usually of the order of 10^{-2}–10^{-3}, and the differences n_1-n_2 are of the order of 10^{-1}–10^{-2}. The discrepancy between the different forms of expressing the concentration depends on the relationship between the properties of the components and often amounts to 10^{-1}, so that the terms $(n_1-n_2)(V_1-N_1)$ and $(n_1-n_2)(V_1-P_1)$ are usually of the same order of magnitude as $\Delta n(V)$.

The magnitude and sign of the deviations from additivity $\Delta n(N)$ and $\Delta n(P)$ depend not only on the behaviour of the components of the mixtures, but also to an equal extent on the relationship between their properties (molar volumes and densities). In real cases

$$|(n_1 - n_2)(V_1 - N_1)| > |\Delta n(V)| , \qquad (2.14)$$

and

$$|(n_1 - n_2)(V_1 - P_1)| > |\Delta n(V)| , \qquad (2.15)$$

and the sign of the deviations from additivity $\Delta n(N)$ and $\Delta n(P)$ is determined entirely by the signs of the differences V_1-N_1 and V_1-P_1, i.e. the signs of these deviations will in such cases depend only on the relationship between the densities and molar volumes of the components:

when $d_2 > d_1$, $V_1 - P_1 > 0$ and $\Delta n(P) > 0$, (2.16)

and when $d_2 < d_1$, $V_1 - P_1 < 0$ and $\Delta n(P) < 0$, (2.17)

when $\frac{M_2}{d_2} < \frac{M_1}{d_1}$, $V_1 - N_1 > 0$ and $\Delta n(N) > 0$, (2.18)

and when $\frac{M_2}{d_2} > \frac{M_1}{d_1}$, $V_1 - N_1 < 0$ and $\Delta n(N) < 0$. (2.19)

From this it follows that the deviations from additivity $\Delta n(N)$ and $\Delta n(P)$ do not in general give direct information about the behaviour of the components of solutions. One of the chief reasons for the many misconceptions and contradictions noted in the previous section is the erroneous formulation of the refractive-index additivity rule (1.1). This may be illustrated by specific examples.

The change in sign of the $n(N)$ curves in pyridine and quinoline systems [30,32] on going from lower to higher carboxylic acids (Fig. 1) is simply explained. It is not related to association of the acids but results merely from the change in the relationship between the molar volumes of pyridine and quinoline (first components) and those of the acids (second components). Fig. 2 shows the calculated $\Delta n(V)$ curves for these systems. In all cases the positive deviation from additivity $\Delta n(V)$ characteristic of irrational systems is observed.

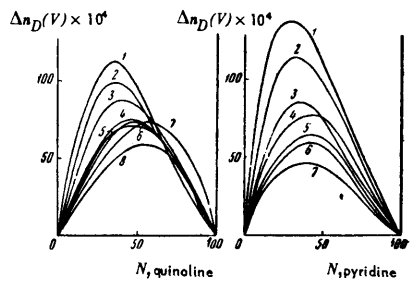


Fig. 2. Deviations from additivity, $\Delta n(V)$ in the same systems as those in Fig. 1.

In the mixtures with the simplest acids, $\frac{M_2}{d_2} < \frac{M_1}{d_1}$, i.e. relationship (2.18) holds, and the positive terms $(n_1-n_2)(V_1-N_1)$, added to the positive quantities $\Delta n(V)$, give extremely high values of $\Delta n(N)$. For the higher acids, $\frac{M_2}{d_2} > \frac{M_1}{d_1}$, and the negative terms at first reduce the positive values of $\Delta n(V)$, leading to the appearance of points of

* Eqns. (2.10) and (2.11) are particular cases of the general algebraic formula for the deviations from additivity of any property Z, regarded as a function of concentrations expressed in the different forms X and Y:

$$\Delta Z(Y) = \Delta Z(X) + (Z_1 - Z_2)(X_1 - Y_1).$$

inflection and afterwards to a change to negative $n(N)$ curves. The change in sign of the $\Delta n(N)$ curves in the pyridine systems takes place earlier than in the quinoline systems, since the molar volume of pyridine is less than that of quinoline.

The marked positive deviations from additivity $\Delta n(N)$ observed in many systems containing non-interacting associated components[46,56] are explained equally simply. These are usually obtained when $\frac{M_2}{d_2} < \frac{M_1}{d_1}$, and this is not related to the nature of the association of the components, as Trifonov and Aleksandrov suggested[46].

The erroneous formulation of the additivity rule (1.1) also explains the misconceptions of Aleksandrov[47] and others regarding the existence of stable molecular complexes in associated components. We have discussed this in detail elsewhere[78].

In the derivation of the additivity rule (2.9), we started from the additivity of specific refractions (2.6). The question arises of whether it is possible to base the choice of additivity rule on direct experiment, independently of the theory of specific or molecular refractions. When claiming linearity for the $n(N)$ isotherms of ideal systems, Anosov[10,12,14] and others referred to the results of the study of certain systems such as mixtures of "iso-fluid" liquids[83]. These systems usually consisted of isomers with very close refractive indices and almost identical molecular volumes (e.g. ethylbenzene and xylenes), so that the terms (n_1-n_2) (V_1-N_1) were very small and the $n(N)$ and $n(V)$ additivity rules (1.1) and (1.3) practically coincided. Experimental data on this type of system naturally cannot be used as argument for the choice of an additivity rule.

In order to make a justifiable choice between the rules (1.1), (1.3), and (1.5) directly based on experimental refractive-index data, it is necessary to examine normal systems made up of components satisfying the conditions

$$n_1 \gg n_2 , \tag{2.20}$$

$$M_1 \gg M_2 \quad \text{or} \quad M_1 \ll M_2 , \tag{2.21}$$

$$d_1 \gg d_2 \quad \text{or} \quad d_1 \ll d_2 , \tag{2.22}$$

$$\frac{M_1}{d_1} \gg \frac{M_2}{d_2} \quad \text{or} \quad \frac{M_1}{d_1} \ll \frac{M_2}{d_2} . \tag{2.23}$$

In addition, in order to avoid erroneous conclusions resulting from an arbitrary choice of systems, it is necessary to examine systems showing all six possible relationships between the properties of the components:

$$\text{I. } P_1 > V_1 > N_1 \left(\text{for } M_1 > M_2,\ d_1 > d_2 \text{ and } \frac{M_1}{d_1} > \frac{M_2}{d_2}\right), \tag{2.24}$$

$$\text{II. } P_1 > N_1 > V_1 \left(\text{for } M_1 > M_2,\ d_1 > d_2 \text{ and } \frac{M_1}{d_1} < \frac{M_2}{d_2}\right), \tag{2.25}$$

$$\text{III. } V_1 > P_1 > N_1 \ (\text{for } M_1 > M_2 \text{ and } d_1 < d_2) \tag{2.26}$$

$$\text{IV. } N_1 > P_1 > V_1 \ (\text{for } M_1 < M_2 \text{ and } d_1 > d_2) \tag{2.27}$$

$$\text{V. } V_1 > P_1 > P_1 \left(\text{for } M_1 < M_2,\ d_1 < d_2 \text{ and } \frac{M_1}{d_1} > \frac{M_2}{d_2}\right), \tag{2.28}$$

$$\text{VI. } N_1 > V_1 > P_1 \left(\text{for } M_1 < M_2,\ d_1 < d_2 \text{ and } \frac{M_1}{d_1} < \frac{M_2}{d_2}\right). \tag{2.29}$$

The results of our studies for all six types[71] are given in Fig. 3, which shows that the additivity rules (1.1) and (1.5) used earlier are incorrect.

In normal systems, the deviations from additivity $\Delta n(N)$ and $\Delta n(P)$ may be very large (0.02–0.03) and it is extremely significant that the magnitude and sign of these deviations have a distinct dependence on the relationships (2.24–2.29) and are therefore determined by the relationship between the molar volumes and densities of the components, and not

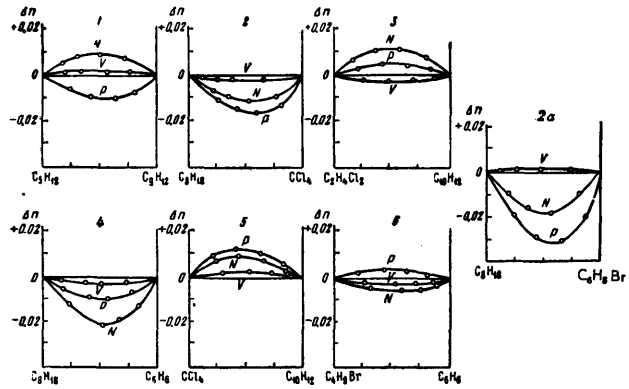


Fig. 3. Deviations of the refractive index from additivity with the composition expressed in mole, N, weight, P, and volume, V fractions in normal systems corresponding to conditions (2.20–2.23): 1) mesitylene–n-pentane; 2) carbon tetrachloride–2,2,4-trimethylpentane; 3) tetralin–dichloroethane; 4) benzene–2,2,4-trimethylpentane; 5) tetralin–carbon tetrachloride; 6) benzene–n-butyl bromide. The numbering of the systems corresponds to relationships I–VI (2.24–2.29).

by their behaviour in mixtures. The values of $\Delta n(N)$ are positive in systems, I, III, and V, where $\frac{M_1}{d_1} \gg \frac{M_2}{d_2}$, and negative in systems II, IV, and VI, where $\frac{M_1}{d_1} \ll \frac{M_2}{d_2}$.

The smallest deviations from additivity in all the cases studied are observed when the concentrations are expressed in volume fractions, corresponding to additivity rule (2.9). Unlike $\Delta n(N)$ and $\Delta n(P)$ the deviations from additivity $\Delta n(V)$ are not connected with relationships (2.24–2.29), and are caused by deviations from ideal behaviour, as shown, in particular, by the change in volume on mixing. The fact that $\Delta n(V)$ is independent of the relationship between the properties of the components is shown very clearly by a comparison of the carbon tetrachloride–2,2,4-trimethylpentane and bromobenzene–2,2,4-trimethylpentane systems. Both systems represent Case II (2.25), and accordingly the $\Delta n(N)$ and $\Delta n(P)$ curves are disposed in exactly analogous fashion. In the first system, where expansion is observed, the $\Delta n(V)$ values are negative, but in the second, where contraction is observed, they are positive.

III. RELATIONSHIP BETWEEN THE DEVIATIONS FROM ADDITIVITY OF REFRACTIVE INDICES, DENSITIES, AND SPECIFIC REFRACTIONS

The above relationship between the deviations from additivity $\Delta n(V)$ and the change in volume is obvious from a physical point of view; the refractive index depends on the number of particles in unit volume and is thus affected by expansion and contraction in the system. This relationship must be studied in more detail when examining the possibility of characterising the behaviour of the components of solutions by the values of $\Delta n(V)$.

The deviations of the refractive indices from additivity in all organic systems (with the exception of a few rational ones) do not exceed 1.0–1.7% of n, and the change in volume

likewise does not exceed a few per cent, so that in order to find the desired relationship we are justified in differentiating the general expression for the specific refraction (2.1) and replacing the differentials by finite increments. In the general case, where the system is non-ideal and deviations of the specific refraction from additivity and volume changes both occur, we have

$$\Delta f(n) = r\Delta d + d\Delta r. \qquad (3.1)$$

When the Gladstone–Dale formula $f(n) = n-1$ is used as a particular case of (3.1), we obtain

$$\Delta n = r\Delta d + d\Delta r. \qquad (3.2)$$

Here, of course, the deviations from additivity Δn, Δd, and Δr signify the deviations from rules which have a physical basis and not from arbitrary ones, i.e. the quantities $\Delta n(V)$, $\Delta d(V)$, and $\Delta r(P)$, so that a more correct form of (3.2) is

$$\Delta n(V) = r\Delta d(V) + d\Delta r(P), \qquad (3.3)$$

where $r = (n-1)/d$.

The particular expression (3.3) is just as rigorous as the general expression (3.1). The approximate character of the Gladstone–Dale equation is shown only in that the quantity Δr in (3.3) includes two effects: the deviations from additivity resulting from the non-ideal nature of the system and the deviations resulting from the inaccuracy of the Gladstone–Dale function. The simple relationship (3.3) makes it possible to reach a number of extremely important conclusions about the reasons for deviations from additivity of refractive indices and the connection between these and physical and chemical processes in solution.

Firstly, it can be seen from (3.3) that there need not necessarily be a simple relationship between the deviations from additivity of the refractive indices and the densities, as claimed by Pulfrich[67] and by a number of authors, up to the present. The sign of $\Delta n(V)$ is determined by the sign of the volume change $\Delta v = -\Delta d/d^2$ only when Δr is sufficiently small and

$$|d\Delta r| < |r\Delta d|. \qquad (3.4)$$

Condition (3.4) is in fact observed in normal systems, and in a large number of systems with associated and interacting components. In systems with contraction, therefore, $\Delta n(V)$ is usually positive, and in systems with expansion, negative*. This is not a strict rule, however, and when condition (3.4) is not fulfilled, cases are possible where compression is accompanied by negative deviations $\Delta n(V)$, and expansion by positive deviations. This has been confirmed experimentally in a number of cases, some of which are dealt with below in connection with the problem of characterising interaction between components from the sign of $\Delta n(V)$.

A very important consequence of relationship (3.3) is that there is no definite relationship between the sign of $\Delta n(V)$ and the nature of the interaction between the components. Positive deviations $\Delta d(V)$ are not always associated with compound formation, and negative deviations $\Delta d(V)$ are not necessarily due to dissociation of associated components[14]. A change in volume may also be observed when normal liquids, which do not interact chemically, are mixed, owing to the inequality of the internal pressures and compressibility coefficients of the components[84], and also to the purely geometrical effect of packing particles of different size and shape.

On the other hand, the deviations from additivity of the refraction $\Delta r(P)$ or $\Delta Mr(N)$ when chemical compounds are formed in a system need not necessarily be positive. For example, the molecular compounds formed by phenols with aromatic amines show a depression of the molecular refraction[85].

These considerations indicate that, contrary to the views of earlier workers, negative refractive-index isotherms may also be expected in systems with clearly defined chemical interaction between the components. Negative deviations from additivity of the refractive indices may be brought about by the compound formation itself, and not as a result of the erroneous formulation of the additivity rule (as in papers by Matavul' [30,40]), nor by the opposite effect of the breakdown of associated molecules. This assertion requires experimental confirmation.

An examination of the literature data for a large number (over 150) binary systems, together with our experiments on systems not previously studied, has shown that negative $n(V)$ curves are in fact encountered in typical irrational systems, such as mixtures of dimethylaniline with acids (formic, isobutyric, and isovaleric) and with *m*-cresol. The results for three of these systems are given in Fig. 4, and show the reasons for the appearance of negative $n(V)$ isotherms. In all three cases, as is usual in irrational systems, contraction takes place $[\Delta d(V) > 0]$. With this condition, in accordance with (3.3), negative values of $\Delta n(V)$ can only be observed if $\Delta r < 0$ and $|r\Delta d| < |d\Delta r|$, and these conditions apply in the systems under study. The marked negative deviations Δr, to which the appearance of negative $n(V)$ isotherms is here related, result directly from chemical interaction of the components. As already mentioned, the formation of molecular compounds by aromatic amines with phenols shows a decrease in molecular refraction compared with the additive values[85]. This depression is related to the hypsochromic shift of the absorption bands of the amines under the influence of acids. In the light of modern views on the relationship between molecular refraction and electronic spectra on the one hand, and the structure of organic substances on the other, these effects shown by aromatic amines are quite understandable. The p-π-conjugated system in aromatic amines, which is associated with exaltation of the refraction and bathochromic

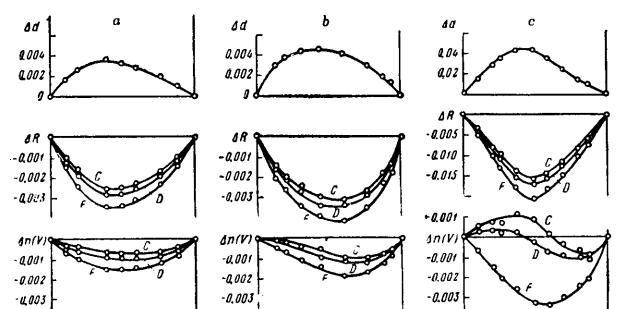
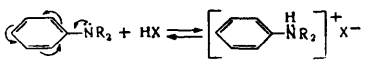


Fig. 4. Negative deviations from additivity of the refractive indices $\Delta n(V)$ molecular refractions ΔR, and densities Δd in the irrational systems (*a*) dimethylaniline–*m*-cresol, (*b*) dimethylaniline–isovaleric acid, and (*c*) dimethylaniline–formic acid, for red (*C*), yellow (*D*), and blue (*F*) light.

* We are here dealing with the quantities $\Delta n(V)$. The deviations $\Delta n(N)$ and $\Delta n(P)$ are not, generally speaking, related to the volume change in a simple fashion. Attempts to affirm such relationships [63,70] are not justified.

shifts of the absorption bands, is destroyed when protons are introduced into the electron clouds of the nitrogen atom. The polarisability of the electrons, in the field of the positive charge, decreases, leading to a hypsochromic shift of the long-wave absorption bands and to marked negative deviations from additivity of the molecular (or specific) refraction:



The above interpretation of the appearance of negative $n(V)$ isotherms in irrational systems is supported by a comparison of mixtures with different amines. The Table gives the maximum (absolute) values of $\Delta n(V)$ for 9 systems of the amine–acid type, and shows that the systems with aniline have large positive $\Delta n(V)$, characteristic of systems involving compound formation. In the methylaniline systems the deviations $\Delta n(V)$ are much smaller, and the $n(V)$ isotherms, although positive, cannot be distinguished from those for normal ones [76]. Finally, in the dimethylaniline systems, the sign of the $n(V)$curves becomes "anomalous" and they are now convex towards the composition axis. The strength of the bases increases in the series: aniline, methylaniline, dimethylaniline, and the degree of association apparently decreases in the same order: the hydrogen bond, which is a factor in association, is absent in dimethylaniline. If therefore we start from the original assumption [14] that compound formation is revealed in positive deviations from additivity (which increase with increase in the strength of the interaction) while breakdown of associated components leads to the opposite effect, then we would expect effects exactly opposite to those actually observed. From the modern viewpoint, the relationships observed in these systems are quite understandable. As a direct consequence of compound formation, the negative deviations appear in mixtures containing the strongest base, dimethylaniline; moreover, this has the greatest exaltation of molecular refraction, which decreases on salt formation. In the case of the weaker base methylaniline, the Δr are smaller and the effect of the contraction predominates.

Maximum (absolute) deviations of the refractive indices from additivity in mixtures of aromatic amines with acids.

Base	Maximum values of $\Delta n_D^{20}(V) \times 10^4$ in systems with the acids		
	formic	iso-butyric	iso-valeric
Aniline	+218	+78	+76
Methylaniline	+46	+27	+30
Dimethylaniline	+2 *	−17	−11
	−111		

* $n_D^{20}(V)$ isotherm positive-negative (Fig. 4).

The dimethylaniline–formic acid system is of particular interest, since here the shape of the refractive-index curves depends on the wave-length of the light. The deviations of r from additivity observed in this case increase on going from the red to the violet region of the spectrum, and are related to the hypsochromic shift of the absorption bands in the near ultra-violet, which is observed on interaction with acids. For the red C rays, at a considerable distance from the violet, the deviation of r from additivity is comparatively

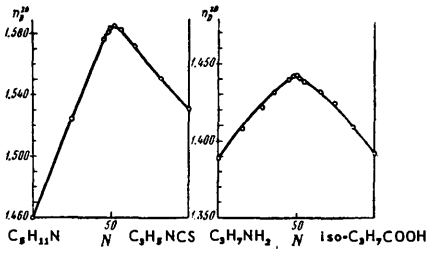


Fig. 5. Examples of singular diagrams for refractive index (piperidine-allyl mustard oil [10] and propylamine-isobutyric acid [31]).

small; the opposite effect of contraction predominates over a wide concentration range, and the $n_C^{20}(V)$ curve is S-shaped, with a change in sign. For the yellow D rays, an exactly analogous picture is obtained, but as a result of the increase in Δr, the negative part of the $n_D^{20}(V)$ curve increases considerably. For the blue F lines, the values of Δr are so high that the $n_F^{20}(V)$ curve is negative at all concentrations and indistinguishable from the analogous curves for mixtures of non-interacting components.

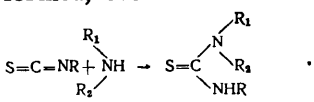
There is thus no simple relationship between the nature of the interaction of the components and the magnitude of the deviations from additivity $\Delta n(V)$. Similarly, in accordance with (3.3), no strict correspondence can be expected between the signs of $\Delta n(V)$, $\Delta r(P)$, $\Delta d(V)$, or $\Delta v(P)$.

IV. UNIQUE POINTS ON REFRACTIVE-INDEX DIAGRAMS

In physicochemical analysis, the unique points on the composition vs. property diagrams are used, in addition to deviations from additivity, to examine the interaction between the components of binary and more complex systems. Until recently, the only kinds of unique point which have figured in work on the refractometric method of physicochemical analysis have been singular points and maximum turning points.

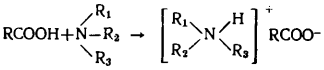
The singular (Daltonide) points have been most studied. These appear when a stable compound, not dissociated into its components, is formed in the system, and they correspond exactly to the composition of the compound. Neither the position of the singular point, nor the very fact of its existence, are dependent on the method of expressing the composition. The singular points so far observed in binary organic systems have been the so-called *angular* points, i.e. points of intersection of two branches of the curve (Fig. 5).

The number of different types of binary systems with a singular point on the refractive-index curves which have been studied is small, all being systems with interaction of the type $A + B = C$. A favourite example of such "rational" organic systems in papers by Kurnakov's school was the combination of primary or secondary amines with isothiocyanates, in which stable (practically undissociated) substituted thioureas, with a marked tendency to undergo supercooling, are formed, even in the cold:



Other examples include certain systems of the aliphatic

amine–carboxylic acid type, in which low-melting substituted ammonium salts, also with a tendency to supercooling, are formed[31,33]:



(R_1 and R_2 = H or alkyl; R and R_3 = alkyl)

Singular refractive-index diagrams for binary systems are of interest chiefly as illustrative material for characterising particular features of composition vs. property diagrams. In organic chemistry, the singular refractive-index curves so far studied have been of little value: the formation of thioureas and substituted ammonium salts are well-known and typical amine reactions.

The maxima on the refractive-index curves were the first unique points to which attention was turned in connection with interaction between components[1], and their appearance was taken as proof of compound formation. The position of the maximum was sometimes taken to correspond to the composition of the compound formed[86], although there were also reports that the maxima of n were displaced considerably towards the component with the higher index and should not be used to deduce the composition of the compound. Although refractive-index maxima have long been known, the conditions for their appearance were examined only recently[74]. The other forms of unique point on the refractive-index isotherms — minimum points and points of inflection — have likewise only been studied in recent years[73,75].

Let us first examine in a general way the conditions for the appearance of maxima and minima in the refractive index. For deviations from additivity of the $f(n)$ function, (2.8), we have the expression

$$\Delta f(n) = f(n)_{exp} - f(n_1)V_1 - f(n_2)V_2 \quad . \tag{4.1}$$

The conditions for turning points of $f(n)$ are obtained by differentiating with respect to V_1 and equating $\partial f(n)/\partial V_1$ to zero:

$$\frac{\partial}{\partial V_1}\Delta f(n) = f(n_2) - f(n_1) \quad . \tag{4.2}$$

This equation is the condition for maximum and minimum values of $f(n)$, but we are interested in the maximum and minimum values on the n isotherms. In order to solve this problem, it is not necessary to choose the best of the proposed molecular (or specific) refraction formulae, since the derivative $\partial f(n)/\partial n$ does not become equal to zero under any set of real conditions, for any of the forms of the function $f(n)$ (2.2–2.5) or for any other proposed refraction formula. Consequently, $\partial f(n)/\partial V = 0$ only when $\partial n/\partial V = 0$. Thus the maximum and minimum values of $f(n)$ must correspond to maximum and minimum values of n, and, if condition (4.2) is fulfilled, maxima or minima should be observed on the refractive-index curves.

Condition (4.2) requires only a definite relationship between the numerical values of the refractive indices of the components n_1 and n_2 and the magnitude of the derivative of the deviation from additivity $\frac{\partial}{\partial V_1}\Delta f(n)$. It contains no limitations associated with the reasons for the deviation from additivity, $\Delta f(n)$. But these deviations from additivity (see 4.1) need not be related to the production of new molecules in the system, and may be due to purely physical (or even geometrical) effects of change in volume. From this it follows that refractive-index maxima and minima may also be obtained in systems without chemical interaction or dissociation of the components, for certain definite numerical relationships between the properties of the components (n, r) and the volume change of the system.

An approximate rule defining the conditions for the appearance of maximum and minimum values of n, and their position, may be obtained using the Gladstone–Dale function (2.2), which satisfies the requirements of additivity satisfactorily; considering the simplest case, where the dependence of the refractive index on the concentration approximates to the parabolic equation $n = a + bV + cV^2$, we have

$$\Delta n(V) = KV_1(1 - V_1) \quad , \tag{4.3}$$

where K is a constant for a given system.

In this case (4.2) becomes

$$V_e = \frac{1}{2} + \frac{n_1 - n_2}{2K} \quad , \tag{4.4}$$

where V_e is the concentration of the first component corresponding to an extremal value of n, and n_1 and n_2 are the refractive indices of the components. In normal systems, where condition (3.4) is fulfilled, the sign of the constant K will be determined by the change in volume of the system. If $K > 0$ (contraction), there will be a maximum, and when $K < 0$ (expansion), a minimum refractive index in the system.

Relationship (4.4) shows that for a given value of K, a maximum value of n will lie closer to the component with larger n, and a minimum value closer to the component with smaller n, by an amount which increases with the difference between the refractive indices of the components.

Taking account of the obvious relationship $0 < V_e < 1$, we find that in case (4.3), the condition for the appearance of maxima or minima of n is

$$|n_1 - n_2| < |K|. \tag{4.5}$$

Examination of the experimental refractive-index data and volume changes for normal systems indicates that K may amount to 0.02. It may thus be expected that maxima or minima in n will appear in normal systems when the refractive indices of the components are sufficiently close: $|n_1 - n_2| < 0.02$.

On the basis of these considerations, it has been possible to detect extremal values of the refractive index in mixtures of hydrocarbons and their halogen derivatives, which are usually included in the class of normal systems[74]. The cyclohexyl bromide–ethylbenzene system has been most studied and illustrates clearly the rule formulated above for the dependence of the displacement of the maxima or minima on the relationship between the properties (refractive indices) on the components. Cyclohexyl bromide and ethylbenzene have widely differing dispersions, so that the difference $n_1 - n_2$ depends to a marked extent on the wavelength: the value for the C lines is 15 times, and that for the F lines 33 times greater than that for the D lines, while for red light, ethylbenzene has the lower n, and for blue, cyclohexyl bromide (Fig. 6). At the same time the value of K (4.3) varies little with wavelength. In accordance with (4.4), the minimum on the n_D^{20} isotherm at 43 vol.% of ethylbenzene is displaced towards ethylbenzene (66%) on the n_C^{20} isotherm, and towards cyclohexyl bromide (10% $C_6H_5C_2H_5$) on the n_F^{20} isotherm. At shorter wavelengths, $n_1 - n_2$ will be even larger and the minimum in n in this system probably disappears.

Comparison of the 15 systems with minimum n known at present [73,74] shows that they contain both strongly associated components (acids and alcohols) and weakly associated or non-associated components (hydrocarbons and their halogen derivatives). Neither the existence of the minimum n, nor its position, nor its value, can be related to the concentration of associated components or to their degree of association. From this it follows that negative deviations of n from additivity (for any formulation) need not be related to dissociation of the components.

Points of inflection are the least studied of the unique points on composition vs. property diagrams. They are most frequently observed on heats of mixing and viscosity curves, in systems with fairly well defined chemical interaction between the components. Their appearance on the diagrams for these properties is usually interpreted as resulting from the formation of compounds of the associated components [13,14]. Unlike singular and turning (extremal) points, points of inflection on property vs. composition curves may appear or disappear according to the method of expressing the composition [14], so that in discussing points of inflection, the choice of the correct method of expressing the composition is of fundamental importance.

Points of inflection on the $n(V)$ isotherms were first considered for the case of S-shaped curves with a change in sign of the deviations from additivity [73,75]. The conditions for the appearance of positive–negative $n(V)$ isotherms may be sufficiently revealed by starting from the expression for the deviations of the refractive index from additivity (3.2):

$$\Delta n(V) = r\Delta d + d\Delta r.$$

Since Δr and $d\Delta r$ are not very large compared with $r\Delta d$, two cases are of practical interest: 1) those where the deviations of the specific refraction from additivity are practically zero; 2) those where the terms $r\Delta d$ and $d\Delta r$ are of the same order of magnitude.

In the first case, as pointed out in the previous section, the sign of $\Delta n(V)$ should be the same as that of the deviations of the densities from additivity and opposite to that of the change in volume, so that in systems where the condition of additivity of r is sufficiently well fulfilled, positive–negative $n(V)$ isotherms can and should appear only when the sign of Δd and Δv changes as the concentration of the components changes.

In the second (more general) case, a change in the sign of $\Delta n(V)$ is obviously possible in systems where the $d(V)$ or $v(P)$ isotherms do not change sign. A necessary condition is that the signs of Δr and Δd should not be the same (or that those of Δr and Δv should be). This condition is not sufficient, however, since it is also necessary that in one concentration range $|r\Delta d| > |d\Delta r|$ and in another $|r\Delta d| < |d\Delta r|$. This last requirement is satisfied when the values of d or r for the components differ appreciably, the greater density corresponding to the lower refraction. These conditions restrict considerably the number of systems in which positive–negative $n(V)$ curves may be expected, and such curves are rare. It has been possible, however, to confirm experimentally all three of the above possibilities for the production of positive–negative $n(V)$ isotherms, and these are shown in Fig. 7.[75]

The case of S-shaped isotherms in systems with contraction at all concentrations and with marked negative deviations of r from additivity is comparatively more common. It is normally found in irrational systems of the

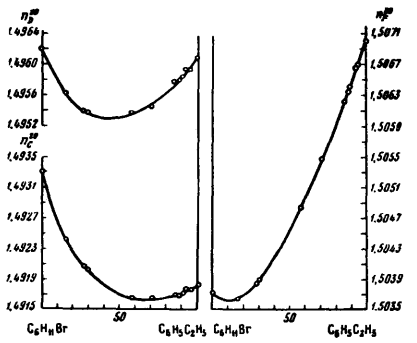


Fig. 6. Position of the refractive-index minima in the ethylbenzene–cyclohexyl bromide system for red (C), yellow (D), and blue (F) light.

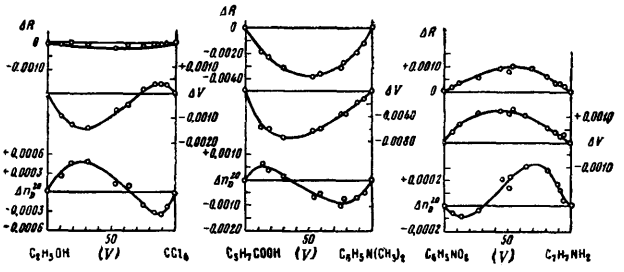


Fig. 7. Three cases of positive-negative $n(V)$ isotherm formation (ethyl alcohol–carbon tetrachloride, dimethylaniline–butyric acid and m-toluidine–nitrobenzene systems).

acid-base type, with aromatic or heterocyclic bases showing marked absorption in the near ultraviolet. Positive–negative $n(V)$ isotherms are encountered not only in irrational systems [75], however, so that points of inflection on the n curves cannot be regarded as sufficient evidence for the formation of compounds in a system.

V. CLASSIFICATION OF REFRACTIVE-INDEX ISOTHERMS

The classification of refractive-index isotherms proposed by Anosov [12–14] assumes that the composition is expressed in mole fractions (percentages). The incorrect choice of this parameter is one of the fundamental reasons for the inapplicability of this classification and its non-correspondence (except for the 4th class of singular diagrams) with observed relationships.

Another reason for the unsuitability of Anosov's classification is the erroneous assumption that the magnitude of the deviations from additivity depends unequivocally on the nature of the behaviour of the components (for example, compound formation could be accompanied only by positive deviations from additivity).

A third reason for errors made in the past in interpreting the shape of the refractive-index isotherms is the complete neglect of all factors influencing the deviations of the refractive index from additivity except the purely chemical

ones. Any deviation from additivity (erroneously formulated, moreover) was ascribed to the production of new molecules in the system and related either to combination of the components or to breakdown of associated molecules to simpler forms.

The new classification of refractive-index diagrams [72] for the physicochemical analysis of binary systems is based on the conclusions given in the previous sections regarding the shape of the refractive-index curves and on the results of examination of the experimental data for almost 200 organic systems.

The classification of all non-singular curves is based on the magnitude of the deviations from additivity with respect to the *volume* fractions of the components, $\Delta n(V)$. Since the earlier qualitative approach to the characterisation of non-singular curves by the direction of their convexity (the sign of the deviations from additivity) is clearly insufficient for any definite differentiation of systems according to their physicochemical character, it is necessary to use some quantitative criterion, such as the roughly quantitative deviations from additivity, as one of the factors for classification.

Examination of the available data shows that in normal systems, and in systems with associated components which do not form compounds, the maximum deviations of the refractive indices from additivity do not exceed +0.007. Higher positive values of $\Delta n(V)$ are encountered only in systems with clearly defined chemical interaction between the components, so that high values of $\Delta n(V)$, greater 0.007, may be taken as fairly conclusive evidence for classifying the system as irrational, in spite of the somewhat arbitrary and approximate nature of this criterion.

It is not possible to find an analogous criterion to detect association of the components. It is evident that even the marked association of components resulting from hydrogen bonding is not reflected distinctly in the refractive-index curves. This conclusion is in accordance with the failure of attempts to detect hydrogen bonds in binary systems containing alcohols and acids from the deviations from additivity of the molecular refractions [87-89].

According to the conclusions of the previous section, the only forms of unique point which may be used as criteria for the formation of compounds are singular points and maximum turning points. The actual existence of a non-singular maximum is proof of compound formation only when the difference between the refractive indices of the components is sufficiently high, i.e. $n_1 - n_2 > 0.02-0.03$; otherwise systems should be classed as irrational not on the basis that a maximum n exists, but on the height of this maximum, i.e. on the value of the maximum deviation from additivity.

For the purposes of physicochemical analysis, therefore, three classes of $n(V)$ curve should be distinguished:

Class I -- isotherms with a small curvature: maximum values of $\Delta n(V)$ positive or negative, but not exceeding +0.007.

Class II — isotherms with a marked convexity away from the composition axis (deviations from additivity $\Delta n(V)$ exceeding 0.007).

Class III — isotherms with a singular point (break), characteristic of systems in which non-dissociated compounds are formed. Since the singular points are preserved on going from mole fractions to volume fractions, this class corresponds exactly to Anosov's Class 4.

Most binary liquid systems have $n(V)$ isotherms of type I, including all normal systems, systems with non-interacting associated components, and also a number of systems with chemical interaction, sometimes fairly strong, but not revealed distinctly on the $n(V)$ curves. Isotherms of Class I may show points of inflection, and possibly maximum or minimum turning points (when the refractive indices of the components are similar, i.e. $n_1 - n_2 < 0.02$).

Class II includes systems with marked chemical interaction and formation of partly dissociated compounds. The isotherms for this class quite often show maxima, and occasionally points of inflection*.

The singular points on Class III diagrams, in almost all known cases, are maximum turning points. Other unique points may be encountered, but only one such case is known — the non-singular maximum in the acetic anhydride—-water system.

This classification includes all available literature data on refraction in binary liquid systems.

VI. THE USE OF REFRACTOMETRY FOR THE STUDY OF INTERACTION BETWEEN COMPONENTS IN BINARY LIQUID SYSTEMS

According to the new classification, it is necessary to distinguish cases where the refractometric data, by themselves, give sufficient proof of compound formation between the components (curves of Classes II and III), from cases where such data alone cannot give definite information regarding the behaviour of the components (curves of Class I). Unfortunately, Class I is the most widespread, and this restricts the independent application of refractometry in physicochemical analysis. Other methods must be used to study systems where the deviations of the refractive indices from additivity are small. In this case, however, we must not restrict ourselves to the traditional comparison of the shape of the property vs. composition curves with isotherm types established empirically, but should examine, in all possible detail, the quantitative relationships between the various properties. An example of such a relationship is Eqn. (3.3), and use of this in the study of curves of Class I reveals, in particular, typical irrational systems in which compound formation is not clearly reflected in the refractive-index curves, as a result of the opposed signs and mutually weakening effects of the non-additivity of the densities and specific refractions.

When the compounds formed are very unstable and their concentrations very low, they can hardly be detected by the refractometric method, for the influence of the negligibly small number of new molecules formed will not be noticed against the other effects. An example is the tetranitromethane–benzene system [77]. When the components are mixed, a fairly intense yellow colour appears and the spectrophotometric curves give distinct proof of the formation of new molecules, although the refractive-index diagrams show no signs of interaction between the components, in spite of the close connection between the refraction and absorption of light. In view of the low concentration of unstable complexes formed, the factor determining the shape of the

* The single case recently described [90] of a refractive-index minimum existing together with a fairly high maximum (in the acetic anhydride – nitric acid system) requires confirmation and explanation.

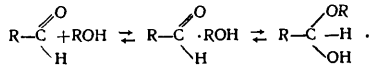
$n(V)$ isotherms is not the deepening of the colour, but the expansion observed in the system.

The position of the singular points or the maximum deviations from additivity (on curves of Class II) can be used to obtain information about the composition of the compounds formed. It must be noted, however, that the position of these points is determined, strictly speaking, not by the composition of the compounds but by the ratio of the stoichiometric coefficients of the equations for the chemical processes taking place in the system. Thus, for example, a singular point may be found at a molar ratio of components of 1 : 1 in combination reactions $A + B = C$ and also in double decomposition reactions $A + B = C + D$. Information on the composition of the compounds may thus be obtained from the position of the singular points or maximum $\Delta n(V)$ if further information is available, or assumptions made, regarding the type of reaction occurring in the system.

The new viewpoint is well based on a more careful interpretation of refractometric data. Recent views [71-79] differ essentially from the basic postulates of earlier work and in many cases lead to a different interpretation and evaluation of the shape of non-singular refractive-index diagrams. Since the many earlier attempts to relate the deviations from additivity $\Delta n(N)$ and $\Delta n(P)$ only to interaction or dissociation of components with different molar volumes and densities must be regarded as fundamentally erroneous, it becomes necessary to re-examine the conclusions reached in earlier work by interpreting $\Delta n(N)$ and $\Delta n(P)$ in this manner*.

As pointed out in Section II, certain conclusions reached by early workers, such as those of Matavul' [30,32] and Aleksandrov [47] regarding the influence of association on the refractive index, are quite incorrect. Certain early data on compound formation in organic systems appear unconvincing when re-examined from the new viewpoint. For example, the data for mixtures of acetone with carboxylic acids [64] cannot be taken as proof of compound formation; another example is the small maximum n_D in the pyrrole—pyridine system [96], where the values of n for the components are similar ($n_1 - n_2 = 0.0013$), which is inadequate to prove that a compound is formed, without the support of other data.

At the same time many of the conclusions reached in earlier work, relating to systems with clearly defined chemical interaction between the components, retain their significance. For example, refractometry has played an important part in solving the problem of hemiacetal formation in aldehyde–alcohol mixtures [5,69,97-99]. Measurement of the change in refractive index with time for these systems not only proves that hemiacetal formation takes place, but also reveals the two-stage mechanism of the process:



Interesting and fairly convincing refractometric data have been obtained for the reaction of acetic acid and its nearest homologues with strong acids (sulphuric, phosphoric, and nitric), in which the carboxylic acids act as bases [35,36,40,41,51].

Most observations on the reactions of amines with phenols and carboxylic acids retain their significance.

The formation of hydrates of organic compounds in many aqueous solutions is also being studied by means of refractive-index curves. In this case, however, the $n(N)$ diagrams previously used give a very distorted, if not always completely erroneous, picture of hydrate formation. Since the molecular volume of water is much smaller than that of organic compounds, the deviations from additivity $\Delta n(N)$ acquire extremely high values which do not correspond to the actual hydration effect.

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In summing-up the discussion of the principles involved in applying refractometry to the study of interaction between the components of liquid systems, we may consider its future prospects. Refractometry is not one of the most sensitivie methods for studying intermolecular interactions, and reveals only comparatively strong interactions where fairly stable compounds are formed. In studying systems where such interaction takes place, refractometry may be extremely useful, and equal in importance to other methods. Since the method is readily available, technically simple, and highly accurate, its use in this field is very convenient. In the present state of our knowledge of specific and molecular refraction, however, refractometry must be regarded as poorly adapted to the study of interactions not accompanied by a marked change in the structure and polarisability of a large number of molecules.

Recognition of these features of the refractometric method should prevent the repetition of earlier mistakes and the publication of inconclusive arguments.

* After the publication of articles [71, 72] drawing attention to the inapplicability of the existing classification of refractive-index diagrams and the $n(N)$ additivity rule, a number of authors [41—45, 91] recognised the need to re-examine the earlier conclusions and went over to the study of $n(V)$ curves. Some recent papers [92-95], however, still deal with $n(N)$ curves from the old point of view.

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THE AROMATIC BOND AND SOME PROBLEMS OF THE STRUCTURE OF AROMATIC COMPOUNDS

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INTRODUCTION

The formula proposed by Kekulé[1,2] for benzene, with alternating double and single bonds, explained many but not all its properties. This formula made it difficult to understand, for example, the specific type of reactivity shown by benzene and the existence of one instead of two *ortho*-isomers[3,4].



For this reason Kekulé later suggested[5] that the double bonds in the benzene ring are not fixed but mobile, i.e. they oscillate rapidly, moving around the ring.

The concept of the oscillation of double bonds as an important distinguishing feature of aromatic compounds was accepted rapidly and held sway for a long time. In subsequent papers it was developed into an orderly system of ideas[6]. This concept explained in particular the identity of the two *ortho*-positions in monosubstituted benzenes. In polysubstituted benzenes and especially in di- and polycyclic aromatic compounds, however, the *ortho*-positions are not equivalent, one being more reactive than the other. This led to the suggestion that in these compounds the possible oscillatory forms possess different stabilities, and therefore, being in dynamic equilibrium, take part to different extents in reaction[7]. Thus the double bonds of such compounds are partly or even completely fixed[8-11].

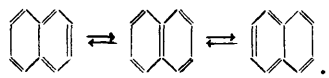
From the progress made in recent years in the study of the fine structure of aromatic compounds it may be concluded that there can be neither oscillation nor complete fixation of the bonds in aromatic molecules.

It has been established by numerous methods that the structure of the benzene molecule is a regular hexagon in which the six π electrons of the carbon atoms do not interact in pairs but as a single sextet. Therefore, all the C – C bonds of benzene are completely equivalent and differ in electron density both from single and from double bonds. From this point of view, Thiele's theory of partial valencies[12] represents the actual structure of aromatic substances better than Kekulé's concept of oscillating bonds. However, many experimental facts indicate that in aromatic compounds other than benzene the C – C bonds are not identical; some of them possess greater electron density, or have greater "double-bond character", than others.

The complete equivalence of the C – C bonds characteristic of the benzene molecule contrasts with the state of these bonds in its derivatives, e.g. di- and polycyclic aromatic compounds. Therefore, it is possible to consider that substituent groups or condensed rings upset to some extent the equivalence of the bonds.

PARTIAL BOND FIXATION

The non-equivalence of the bonds in aromatic compounds was first studied in the case of naphthalene. By analogy with the Kekulé dynamic structure for benzene, the naphthalene molecule can be represented by dynamic formulae[13,14], on the basis of which it might be supposed that the bonds in naphthalene would be equivalent:

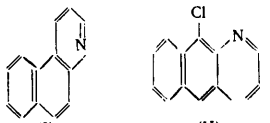


However, many observations indicate the great difference in properties between the 1 – 2 and 2 – 3 bonds. For the sake of clarity, these observations are classified below according to the types of reactions studied.

Cyclisation Reactions and Reactions Occurring via the Intermediate Formation of Rings

As early as 1893 Markwald[15-17] noted the considerable reactivity of one of the two *ortho*-positions in β-naphthol and β-naphthylamine. Thus, when the Skraup reaction is carried out with β-naphthylamine, only the angular benzoquinoline (I) is obtained. In a number of cases formation of I is accompanied by displacement of a substituent present in position 1 of the 2-naphthylamine molecule. According to

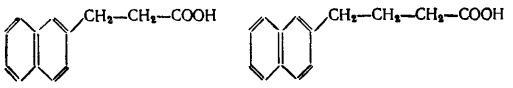
Markwald the reason for this phenomenon was that formation of the new ring occurs at the double bond, and hence that in naphthalene the 1–2 bond is double but the 2–3 bond is single, and this distribution of the bonds is fixed. However, as was shown subsequently[18-20], this course of the Skraup reaction with formation of the benzoquinoline (I) is not the only possible reaction. With certain derivatives of β-naphthylamine, products of linear structure also can be obtained, in moderate yield, e.g. II.



(I) (II)

In the Skraup reaction a certain similarity of behaviour is observed between derivatives of naphthalene and of its heterocyclic analogues, e.g. quinolines[21].

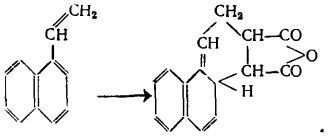
When β-2-naphthylpropionic (III) and γ-2-naphthylbutyric (IV) acids[22-25] are cyclised,



(III) (IV)

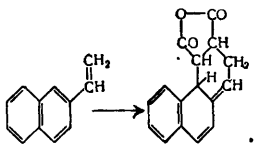
products of angular structure are formed exclusively, although here too, if position 1 is occupied, cyclisation can occur in position 3 [26].

Derivatives of naphthalene also behave peculiarly in diene synthesis reactions[27-30]. 1-Vinylnaphthalene (V) exhibits diene properties, giving with maleic anhydride the corresponding adduct (VI):



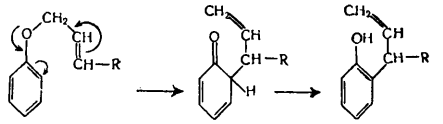
(V) (VI)

Thus the 1–2 bond in the naphthalene molecule behaves in this reaction as a double bond[31-33]. In the case of 2-vinylnaphthalene (VII), the reaction could involve either position 1 or 3. It was shown that the product is formed entirely by reaction at position 1 [34] (VIII):

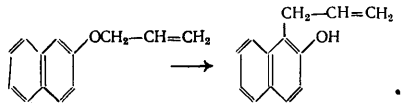


(VII) (VIII)

The non-equivalence of the bonds was also studied by means of the Claisen rearrangement[35,36], by which allyl ethers of phenols and enols are converted into the corresponding *C*-allyl derivatives. The reaction evidently occurs via the intermediate formation of cyclised products and dienes, and with isomerisation of the allyl radical[37,38]:



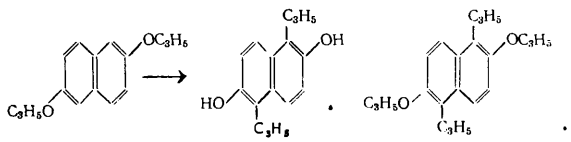
According to this mechanism two double bonds take part in the reaction, and on this basis it is suggested that the process entails fixation of the bonds of the aromatic nucleus. Rearrangement of 2-allyloxynaphthalene (IX) occurs solely at position 1, with formation of X:



(IX) (X)

1-Allyloxynaphthalene is similarly smoothly converted into 2-allyl-1-naphthol; this shows that the direction of the rearrangement IX → X cannot be explained by increased reactivity of the 1-position of naphthalene. If the 2-allyloxynaphthalene (IX) has a substituent in position 1, the Claisen rearrangement does not occur, although position 3 is free[35]. On this basis it can be concluded that the 2–3 bond of naphthalene, in contrast to the 1–2 bond, cannot function as a double bond.

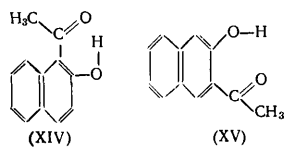
It is known also that, whereas 2,6-diallyloxynaphthalene (XI) rearranges smoothly to 1,5-diallyl-2,6-dihydroxynaphthalene (XII), 1,5-diallyl-2,6-diallyloxynaphthalene (XIII) is not capable of such a rearrangement. This confirms that the partial bond fixation in naphthalene is symmetrical. Naphthalene derivatives do not enter into reactions which require the presence of double bonds in the 2–3 and 6–7 positions[9]:



(XI) (XII) (XIII)

Further investigations of the Claisen rearrangement, pointing to the non-equivalence of the bonds, were carried out with derivatives of anthracene[40], phenanthrene[41], and certain heterocyclic aromatic compounds[42-45].

In 1934, Baker[46] noted that the ability of *o*-hydroxyacetophenone and similar compounds to form six-membered chelate rings containing a hydrogen bond depends on the presence of a double bond between the carbon atoms linked to the hydroxyl and acetyl groups. If it is assumed that only the 1–2 bond in the naphthalene nucleus can behave as a double bond, 1-hydroxy-2-acetylnaphthalene and 2-hydroxy--1-acetylnaphthalene (XIV) should be able, but 2-hydroxy--3-acetylnaphthalene (XV) should be unable, to form a hydrogen bond:



(XIV) (XV)

Actually, a hydrogen bond is present in all three compounds[47]. This could mean that the 2–3 bond can function as a double bond. However, as the authors remark, such a conclusion is not definitive, since the formation of the hydrogen bond itself may change the normal state of the bonds in the molecule[48-51].

Infra-red spectra of nitronaphthylamines show that the 1,2- and 2,1-isomers contain a stable hydrogen bond, whereas no such bond has been detected in the 2,3-isomer[52].

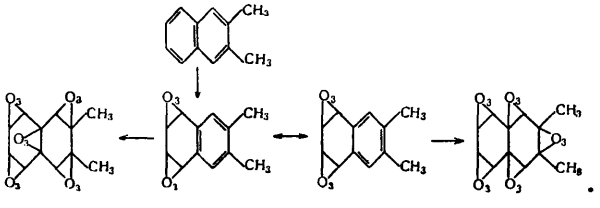
Substances which React with a Double Bond

Interesting and convincing results were obtained in the study of the structure of aromatic compounds by their reaction with substances which can add on to double bonds — ozone, osmium tetroxide, and aliphatic diazo compounds[53]. In the reaction of compounds containing double bonds with ozone, ozonides are obtained[54], the structure of which has not yet been finally elucidated[55].

With benzene, ozone forms a triozonide[56,57]. Levine and Cole studied the ozonisation of *o*-xylene and obtained a mixture of products[58]. Later Haaijman and Wibaut determined the quantitative composition of this mixture, which contained glyoxal, methylglyoxal, and diacetyl, and came to the conclusion that it corresponds strictly to an equilibrium mixture of two isomeric *o*-xylenes having fixed bonds[59,60]. Since such isomers do not exist, these results obviously indicate that all the bonds in *o*-xylene are equivalent. Thus, although the presence of methyl groups does accelerate the ozonisation of benzene derivatives[61], it does not have an appreciable effect on the comparative reactivity of its individual bonds.

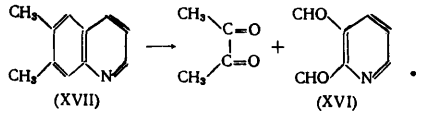
The ozonisation of 2,3-dimethylpyridine and 2,3,4-trimethylpyridine[62] yields a mixture of glyoxal, methylglyoxal, diacetyl, formic and oxalic acids, and ammonia. This also is explained by the pyridine reacting with ozone in the form of two Kekulé structures. From the present point of view this can be treated as proof of the equivalence of the double and single bonds in pyridine.

Ozonisation was also used to study the structure of naphthalene. In 1904 Harries and Weiss obtained phthalic dialdehyde by this reaction[63]. Considerably later, in 1946, Wibaut and Dijk studied the ozonisation of 2,3- and 1,4-dimethylnaphthalene[10]. The former yielded glyoxal, diacetyl, and, what was especially important, methylglyoxal. The ratio of methylglyoxal to diacetyl was 1 : 10. This result was at first treated as a proof that the 2–3 bond of naphthalene can react as a double bond. Then, an apparently more correct explanation was given by Kooyman[64], who considered that this reaction also initially involves the 1–2 and 3–4 bonds, but not the 2–3 bond. The formation of methylglyoxal takes place in the second stage, as a result of further reaction of an intermediate product, in which there is no longer the disruption of bond equivalence characteristic of naphthalene:



The formation of methylglyoxal from 1,4-dimethylnaphthalene can be explained in the same way.

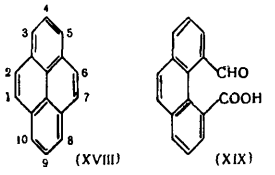
In the reaction of quinoline with ozone[65] a diozonide is formed at the expense of the bonds in the benzene nucleus, and it is only with difficulty that this reacts further with ozone. Decomposition of the diozonide yields glyoxal and pyridine-2,3-dialdehyde (XVI). The products of the ozonisation of 6,7-dimethylquinoline (XVII) are diacetyl and pyridine-2,3-dialdehyde; methylglyoxal and pyridone are not observed:



(XVII) (XVI)

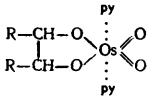
In the ozonisation of 5,8- and 2,3-dimethylquinolines reaction also occurs at the 5–6 and 7–8 bonds, but not at the 6–7 bond, which behaves as a single bond.

The ozonisation of several polycyclic aromatic compounds has also been studied. Anthracene forms only anthraquinone[66]. Pyrene (XVIII) adds on ozone successively at the 1–2 and 6–7 bonds[67,68]. On decomposition of the ozonides, 4-formylphenanthrene-5-carboxylic acid (XIX)[69,70] and the corresponding diphenyl derivative were obtained. It may be noted here that electrophilic reagents, in contrast to ozone, attack in the first instance the very unsaturated[67] positions 3, 5, 8, and 10 in pyrene.



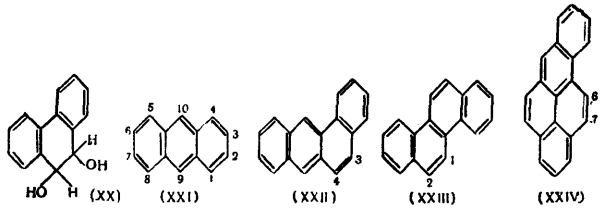
(XVIII) (XIX)

Osmium tetroxide is a considerably milder reagent than ozone. When it interacts in pyridine solution with compounds containing a double bond, crystalline products of the following structure generally separate in theoretical yield:



On careful hydrolysis, diols are obtained from them, and these are often the products required[71,72].

Osmium tetroxide reacts very slowly with aromatic compounds, and adds on only to the most reactive bonds[73]. Thus, with benzene reaction can occur only under extreme conditions[74], and usually it does not occur. Phenanthrene reacts with osmium tetroxide at the 9–10 bond, and after decomposition of the complex *cis*-9,10-dihydroxy-9,10-dihydrophenanthrene (XX) is obtained[71]. Anthracene (XXI) reacts at the 1–2 and 3–4 bonds, giving an addition product containing two molecules of OsO_4.[75] 1,2-Benzanthracene (XXII) adds on osmium tetroxide at the 3–4 bond[73,76], chrysene (XXIII) and pyrene (XVIII) at the 1–2 bonds, and 4,5-benzopyrene (XXIV) at the 6–7 bond[73].

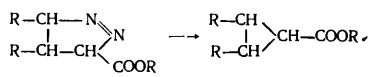


(XX) (XXI) (XXII) (XXIII) (XXIV)

The bonds in polycyclic aromatic compounds possess differing reactivity with respect to OsO_4. Quantitative investigations show, for example, that osmium tetroxide adds on to 1,2-benzanthracene (XXII) ten times as rapidly as to phenanthrene[77]. The presence in the 1,2-benzanthracene molecule of an electron-donor substituent (a methyl group) accelerates the addition of OsO_4, but an

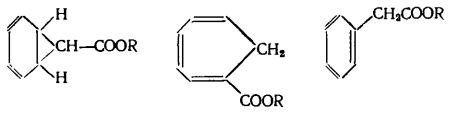
electron-acceptor substituent (a CN group) retards it[78,79].

To elucidate the nature of the aromatic bond, the action of aliphatic diazo compounds — diazoacetic ester and diazomethane — on various compounds was studied. Diazo compounds add on to a double bond, forming pyrazolines, which eliminate nitrogen on mild heating, passing into derivatives of cyclopropane[80-82]:



Diazoacetic ester and diazomethane react with aromatic compounds only with difficulty, and nitrogen is eliminated even before the addition. It has been suggested that the active agent in this reaction is the CH_2 radical[83]. The reaction can also be carried out without heating, using activation with ultra-violet radiation[84].

The reaction of diazoacetic ester with benzene derivatives was studied by Buchner[85-89], who established that the primary product of this reaction is norcaradienecarboxylic ester (XXV), which can undergo further rearrangement to cycloheptatrienecarboxylic (XXVI) and phenylacetic (XXVII) esters.



(XXV) (XXVI) (XXVII)

Reactions with methylated benzenes can also yield phenylpropionic acids. Diazomethane reacts in a similar way. Substituted benzenes always add on diazomethane at a bond between unsubstituted carbon atoms[90].

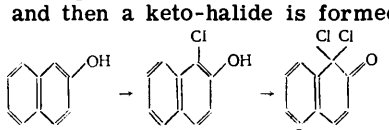
Naphthalene adds on diazoacetic ester at the 1–2 bond[91], phenanthrene at the 9–10 bond[92,93], anthracene at the 1–2 bond[94], benzanthracene (XXII) at the 3–4 bond, and pyrene (XVIII) at the 1–2 bond[95], the products obtained being unable to undergo rearrangement.

The cyclopropane ring is regarded as capable of conjugating with double bonds, and as a result the addition products obtained contain no isolated double bonds[96]. This evidently explains why reactions with diazo compounds terminate at the stage in which these products are obtained.

Substitution Reactions and Transmission of Conjugation Effect

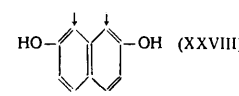
It is well known that the more unsaturated an aromatic bond, the more completely the conjugation transmitted by it. Hence by studying the direction of substitution reactions in aromatic compounds and the readiness with which they occur it can be judged whether and to what extent the equivalence of the bonds in a compound has broken down.

Markwald and then Fries and Fieser discovered a large degree of similarity in the halogenation and coupling of certain phenols and aliphatic enols. For example, in the halogenation of 2-naphthol the first halogen atom enters position 1[97], and then a keto-halide is formed[98-101]:



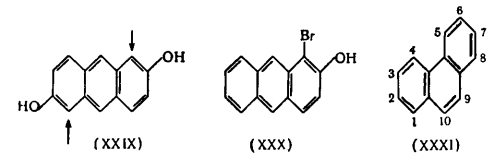
A halogen atom does not enter position 3.

Further, 2-naphthol and its derivatives undergo azo coupling solely in position 1. If this position contains chlorine, bromine, carboxyl, an aldehyde group, a carbinol residue, a sulphonic-acid group, or certain others[102], the coupling reaction involves elimination of these substituents. 1-Alkyl-2-naphthols, however, do not react. On the basis of these data it is suggested that in naphthalene the conjugating effect of a 2-hydroxyl group is readily transmitted to position 1, but not to position 3, since the 2–3 bond approximates to a single bond. Ruggli[103] showed that 2,7-dihydroxynaphthalene (XXVIII) couples with diazonium compounds in positions 1 and 8, which indicates the symmetrical nature of the partial bond fixation in the two rings of naphthalene. If positions 1 and 8 in 2,6-dihydroxynaphthalene are blocked by alkyl groups, azo coupling does not occur even with very reactive diazonium compounds[104].



(XXVIII)

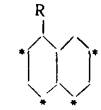
The same methods were used to study the properties of hydroxy derivatives of anthracene, phenanthrene, pyrene, and other compounds. For example, it was established that 2,6-dihydroxyanthracene (XXIX) is brominated in positions 1 and 5[105], 1-bromo-2-hydroxyanthracene (XXX) couples in position 1 with elimination of the bromine atom[106], and 1,5-dialkyl-2,6-dihydroxyanthracenes do not couple with diazonium compounds[40].



(XXIX) (XXX) (XXXI)

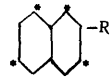
It follows from these observations that in anthracene the 1–2, 3–4, 5–6, and 7–8 bonds are close to double bonds in character, but the 2–3 and 6–7 bonds approximate to single bonds. Similarly, in phenanthrene (XXXI) the 1–2 and 3–4 bonds approximate to double bonds, but the 2–3 bond is close to a single bond[41].

Other experimental evidence exists showing that a substituent in position 2 in naphthalene and its analogues conjugates with position 1, but has hardly any effect on position 3. Substitution in the naphthalene rings to a certain extent obeys the rules formulated by the Czech scientists Vesely and Jakeš[107], according to which a substituent already in the naphthalene molecule exerts an effect at the "quinonogenic" positions, i.e. at positions corresponding to possible naphthaquinones. The effect of the substituent is strongest in the ring containing it. Thus in the case of a 1-substituted naphthalene the substituent will exert an effect at the positions denoted by asterisks:



The effect will be transmitted strongly to positions 2 and 4, and more weakly to positions 5 and 7.

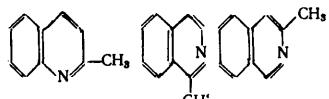
In a 2-substituted naphthalene, the effect of the substituent should also be transmitted to the "quinonogenic" positions:



It would appear that in this case positions 1 and 3 should be

most influenced by the substituent, and positions 6 and 8 to a less extent. In fact this rule breaks down for position 3. Thus in the sulphonation of 2-naphthol position 1 is the most active (according to the rate of entry of the sulphonic-acid group), then follow positions 8 and 6, and position 3 comes only after these[108]. It is known that in the benzene series a nitro group *ortho* or *para* to a halogen increases the lability of the latter. In the naphthalene series the bromine atoms in 1,2-, 2, 1-, and 1,4-bromonitronaphthalenes are labile, but not that in 2,3-bromonitronaphthalene[109]. It is also interesting to trace the effect of an *ortho* substituent on the basicity of amines. *o*-Nitroaniline is considerably less basic than aniline, and 1-nitro-2-naphthylamine than 2--naphthylamine, but the basicity of 3-nitro-2-naphthylamine is only slightly less than that of 2-naphthylamine[110].

Analogous rules can be traced also in the heterocyclic series. According to the Porai–Koshits rule[111,112], the hydrogen atoms of a methyl group are labile if the methyl group is conjugated with the hetero atom. Thus the hydrogen atoms of the CH_3 group in 2-methylquinoline (XXXII) are labile[113]. They are reactive also in 1-methylisoquinoline (XXXIII)[114], but not in 3-methylisoquinoline (XXXIV).



(XXXII) (XXXIII) (XXXIV)

This indicates that in the last compound there is no conjugation between the hetero atom and the methyl group. Thus the 2–3 bond in isoquinoline approaches a single bond in character, but the 1–2 bond is close to a double bond.

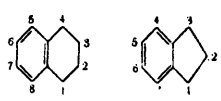
The experimental results given in this section demonstrate convincingly that the carbon–carbon bonds in aromatic systems containing condensed rings are not equivalent. Some of them are similar in character to aliphatic double bonds, and others resemble single bonds. Systems of this type clearly exhibit a phenomenon which can be described as partial bond fixation. The causes of this will be analysed below.

THE MILLS–NIXON EFFECT

In 1930 Mills and Nixon[115] published an investigation which for a long time attracted the constant attention of chemists and gave rise to a great controversy, which was settled only comparatively recently[116,117]. The basis for the theoretical ideas was the suggestion that in ethylene the angle between two single bonds α should be 109.5°, but the angle between a single bond and the double bond β should be 125.25°:

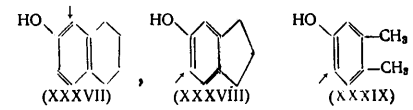


Since a regular hexagon has an angle of 120°, and a pentagon one of 108°, Mills and Nixon suggested that the bond common to the two rings of the tetralin molecule (XXXV) should be double, but the corresponding bond in indane (XXXVI) should be single.



(XXXV) (XXXVI)

In other words, the benzene ring should be fixed in one of its Kekulé forms in tetralin, and in the other Kekulé structure in indane. In fact, by studying the bromination and azo coupling of 6-hydroxytetralin (XXXVII) and 5--hydroxyindane (XXXVIII), Mills and Nixon were able to establish that these reactions occur at position 5 in the first case, and at position 6 in the second case, as would be expected from the formulae



(XXXVII) (XXXVIII) (XXXIX)

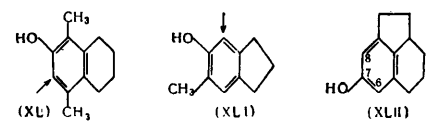
This phenomenon is now known as the Mills–Nixon effect.

On the basis of modern views of the structure of the benzene molecule the Mills–Nixon effect can be treated only as a more or less strong disturbance of the equivalence of the bonds in the benzene ring, occurring under the influence of distortion of the valency angles. In indane this disturbance of bond equivalence tends to give structure XXXVI, and in tetralin structure XXXV. However, on this basis, too, the existence of the Mills–Nixon effect was subject to serious doubts.

Thus it remained obscure why 4-hydroxy-*o*-xylene (XXXIX) couples in the same way as 5-hydroxyindane[118], although there would appear to be no reason for assuming non-equivalence of the bonds in XXXIX. If position 5 in 4-hydroxy-*o*-xylene is occupied by a methyl group, the resulting 2,4,5-trimethylphenol couples smoothly in the other, free *ortho*-position[119]. The comparative reactivity of the two *ortho*-positions in the 4-hydroxy-*o*-xylene molecule (XXXIX) was also determined, by substituting methyl groups in them in turn. The difference in reactivity between positions 3 and 5 proved to be comparatively small[120].

A more detailed investigation of the chemical properties of derivatives of indane and tetralin also showed lack of agreement with the hypothesis of Mills and Nixon. Thus, although 6-hydroxytetralin (XXXVII) couples and is brominated in position 5, it is nitrated in position 7.[121] If the Skraup reaction is carried out with 6-aminotetralin, ring closure also occurs in position 7 and a product of linear structure is formed[122]. 5-Aminoindane, however, undergoes ring closure in the Skraup reaction at position 6.[123]

Fieser and Lothrop discovered that 6-hydroxy-5,8-dimethyltetralin (XL) couples smoothly with diazonium compounds in position 7,[119,120] but 5-hydroxy-6-methylindane (XLI), in a moderately alkaline medium, couples in position 4,[125] which is evidence of the absence in these compounds of any non-equivalence of bonds similar to that observed in the naphthalene molecule.



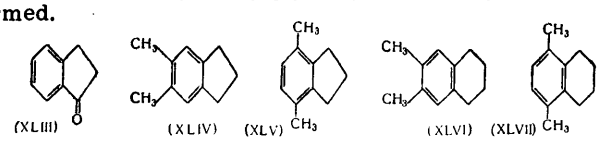
(XL) (XLI) (XLII)

In derivatives of tetrahydroacenaphthene (XLII), in which two saturated rings, one five-membered and the other six-membered, would be acting together, and therefore should influence the state of the bonds in the benzene nucleus more strongly, no naphthalene-like fixation is observed: 7-hydroxy-, 8-hydroxy-, and 7-hydroxy-6-methyl--tetrahydroacenaphthene couple equally smoothly with diazonium compounds[126]. Absence of bond fixation was established by an investigation of the Claisen rearrangement

of 5-allyloxy-6-methylindane and 5-allyloxy-4,7-dimethylindane. Both these compounds rearranged without any difficulty[125]. In the rearrangement of the allyl ether of 6-hydroxytetralin the allyl group rearranges to position 7, not to position 5, as would be expected according to Mills and Nixon. If position 7 is occupied, the allyl group goes into position 5.[127]

Other methods of investigation also show that there is no bond fixation in indane and tetralin. Thus 4- and 6-acetyl--5-hydroxyindane are intramolecularly hydrogen bonded[128]. The acid dissociation constants of 4- and 6-nitro-5-hydroxyindanes and 5-nitro-4-hydroxy-*o*-xylene are almost identical[129], and the heats of hydrogenation of alkylbenzenes and indane are very similar[130].

Important results were obtained in a study of the action of double-bond reagents on indane and tetralin. Arnold[131] established that diazoacetic ester adds to indane at the 4–5 bond, not the 5–6 bond, as would follow according to the theory of Mills and Nixon. The action of ozone on indane was first studied by Young and Fieser[132]. It was found that this reaction starts with the oxidation of indane to indanone (XLIII), and therefore the results obtained are unreliable. The work was then continued by de Jong[133], who studied the ozonisation of 5,6- and 4,7-dimethylindanes (XLIV and XLV) and also 6,7- and 5,8-dimethyltetralins (XLVI and XLVII), and determined quantitatively the proportions of glyoxal, methylglyoxal, and diacetyl thus formed.

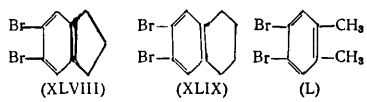


If the Mills–Nixon hypothesis is correct, one mole of compound XLIV should yield two moles of methyglyoxal, but if there is no bond fixation, the ratio of methylglyoxal to diacetyl should be 2 : 1. In fact, the ratio of products obtained is 17 : 6, which by the usual calculation shows a content of molecules having the Mills–Nixon bond fixation of only 15%. Similar treatment of 4,7-dimethylindane (XLV) leads to the conclusion that the proportion of such molecules here is 24%. Using the same method of calculation, it can be concluded from the results of these experiments that, on an average, every molecule of indane having the distribution of bonds indicated in XLIV is accompanied by four molecules with a different arrangement of bonds. This result is just the opposite of what should be observed according to the Mills–Nixon hypothesis. Moreover, these data are in good agreement with the results of theoretical calculations for the indane molecule carried out in 1949 by Longuet–Higgins and Coulson[134,135]. These calculations show that the benzene ring in indane is very slightly distorted in the opposite direction to that postulated by Mills and Nixon: the length of the contiguous 8–9 bond is shortened by 0.022 Å in comparison with that in benzene, and the 5–6 bond is 0.011 Å longer.

On ozonisation of the tetralin derivatives XLVI and XLVII, mixtures of products are obtained, indicating the absence of any bond fixation in their benzene rings. These results are in agreement with theoretical calculations for the tetralin molecule carried out by de Jong on the assumption that the C_2 and C_3 atoms in the alicyclic six-membered ring of this compound are in the *trans*-position with respect to the plane of the benzene ring. The Mills–Nixon effect was also studied in the benzene[136] and pyridine[137] series by means of the ultra-violet and infra-red spectra. The results show the absence of any bond fixation in both cases.

The same conclusion follows from a comparison of the oxidation–reduction potentials of the quinones of indane and tetralin[138]. Thus, all the experimental and theoretical data existing at the present time contradict the existence of the Mills–Nixon effect.

As has already been pointed out, the basis for the Mills–Nixon hypothesis was the assumption that the angles between the single bonds in the ethylene molecule are smaller than those formed between a single and the double bond. Data which have accumulated at the present time[139-142] show that in fact this is not so: all angles in ethylene are very close to 120°. Therefore, although the "linking" of the methyl groups of *o*-xylene by means of one or two methylene groups (formation of a five- or six-membered ring) can somewhat distort the direction of the bonds emerging from the benzene nucleus (especially in the case of indane), this distortion does not affect the state of the bonds in the benzene ring in the Mills–Nixon sense. For a discussion of this question in connection with measurement of the dipole moments of 4,5-dibromoindane (XLVIII, μ = 1.78 *D*), 5,6--dibromotetralin (XLIX, μ = 2.11 *D*), and 4,5-dibromo-*o*--xylene (L, μ = 2.13 *D*), see the papers cited at the end of this review[143-146].



Distortion of the valency angles diminishes the effect of the methylene groups, as electron-donor substituents, on the benzene ring, and therefore this is appreciably smaller with indane than with tetralin. Arnold and his coworkers[147-151] showed this by various experiments. Perhaps this distortion is the actual cause of the different behaviour of 5--hydroxyindane (XXXVIII) and 6-hydroxytetralin (XXXVII) toward coupling with diazonium compounds[133,152-155].

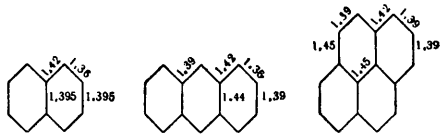
CARBON–CARBON BOND LENGTHS

The above chemical and physicochemical data relating to the difference in the properties of the carbon–carbon bonds in aromatic molecules containing condensed rings have received important confirmation during the past decade from direct determination of C–C bond lengths in such substances.

Several methods exist for the experimental determination of interatomic distances; the most important for organic molecules are those based on the diffraction of X-rays by crystals or the diffraction of electrons by gases. The best results are given by Fourier analysis of the X-ray diffraction patterns, which previously was used comparatively rarely owing to the labour involved in the calculations, but now, with the development of computer techniques, is employed much more widely.

As is known, the length of the single C–C bond is 1.54 Å, that of the double bond in ethylene is 1.34 Å, and that of the triple bond in acetylene 1.2 Å. The C–C bonds of benzene occupy an intermediate position between a single and a double bond, all being alike and 1.39 Å in length. In molecules of polycyclic aromatic hydrocarbons and heterocycles of aromatic character, however, the lengths of all the bonds are not the same[156]. As an illustration, the accompanying formulae show the experimental

interatomic distances for naphthalene[157,158], anthracene[159], and pyrene[160].

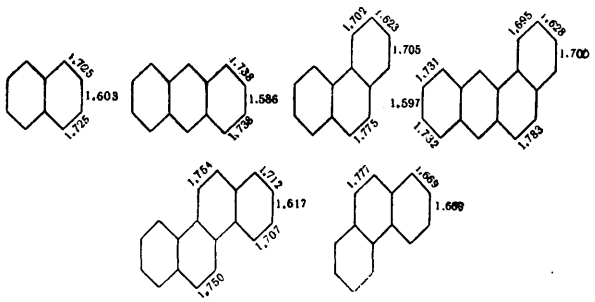


Analogous results have been obtained for the interatomic distances in coronene[161], ovalene[162,163], 1,12-benzoperylene[164], 1,2,5,6-dibenzanthracene[165], triphenylene[166], and a number of other compounds.

These results show that single and double bonds do not exist in polycyclic aromatic hydrocarbons any more than they do in benzene. From the interatomic distances, all bonds are intermediate between single and double bonds. However, some of them, those which in the preceding treatment were regarded as fixed double bonds, are somewhat shorter and therefore closer to double bonds; whereas others, previously regarded as fixed single bonds, are rather longer, and are obviously closer in character to single bonds.

THE ORDER OF AN AROMATIC BOND AND ITS REACTIVITY

The intermediate, non-integral character of the aromatic bond can be established by quantum-mechanical calculations on organic molecules. In the molecular-orbital method, it is assumed that the order of the C–C bonds in ethane is 1, that in ethylene is 2, and that in acetylene 3[142,167,168]. The C–C bonds in aromatic systems are then characterised by fractional orders. Thus the order of all the C–C bonds in benzene is calculated as equal to 1.667, and that in graphite as 1.530. Some results for the calculated order of C–C bonds in aromatic hydrocarbons with condensed rings, calculated by the molecular-orbital method, are shown in the formulae below[169-171].



Analogous results were obtained also in the calculation of the C–C bond orders for anthra-anthracene, dibenzopyrene[172], tetrabenzonaphthalene, tetrabenzanthracene[173], dibenzophenanthrene[174], coronene, ovalene, circumanthracene[175], and a number of other hydrocarbons, as well as heterocyclic compounds[176].

Without attempting in this paper to give a summary of work on the quantum-mechanical calculations on organic molecules, it is pointed out that apparently completely satisfactory results are given by the tabular method, based on an examination of the purely geometrical properties of the molecules, which enables the order of the C–C bonds in aromatic molecules to be found without complicated calculations[177-179].

Application of the linear combination of atomic orbitals (L. C. A. O.) with self-consistent field treatment to the calculation of the naphthalene molecule gives bond orders differing appreciably in magnitude from those given above[180]. This method generally gives too high values for the highest bond orders, and too low values for the lowest bond orders[179].

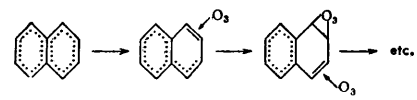
The work of Bykov is worthy of attention, as he proposed the use of electron densities instead of conventional bond orders to characterise chemical bonds. He gave semi-empirical formulae which enabled the latter to be readily calculated from the interatomic distances[181-183]. The electron density of a bond and its order should, of course, be related in a simple manner.

Thus all results show that the various C–C bonds in aromatic compounds differ from one another in their order and electron density. Bonds having a higher order are the most reactive chemically. They add ozone, osmium tetroxide, and diazoacetic ester more readily than do the remaining bonds. In older work they were taken to be fixed double bonds, since in many reactions they behave like actual double bonds. The higher the order of a bond the more reactive it is, and the more it resembles a double bond. An example is the reaction of osmium tetroxide with phenanthrene and 1,2-benzanthracene, already mentioned, which is ten times slower with the former hydrocarbon than with the latter. Correspondingly, the order of the 9–10 bond in phenanthrene is 1.775, and that of the 3–4 bond in 1,2-benzanthracene is 1.783.

1-Nitro-2-naphthylamine is far less basic than 3-nitro-2-naphthylamine, because the effect of the conjugation of the nitro groups is transmitted more completely through the 1–2 bond, which has an order of 1.725, than through the 2–3 bond, the order of which is 1.603. For the same reason, the Claisen rearrangement of the allyl ether of 2-naphthol and the azo coupling of 2-naphthol occur in position 1, and not in position 3, etc.

To show the physical reality of these bond orders, it should be mentioned that they are related to the interatomic distances by a smooth curve[169,184], as shown in Fig. 1[184]. Conversion from bond orders to bond lengths is also easily accomplished by means of the Deas relationship[185,186].

The relationship between the order of a bond and its reactivity is of the greatest importance for chemistry and should therefore be examined more fully. Evidently the start of the process of addition of reagents to an aromatic bond is the conversion of the latter into an actual double bond[187]. This means that two π electrons must be removed from the general π-electron system of an aromatic compound and localised, and the remaining electrons should regroup to form a system with minimum energy. For example, the addition of ozone to naphthalene can be illustrated by the scheme



The energy required to achieve such localisation, termed the localisation energy of the bond, can be easily calculated by the methods of quantum mechanics. Thus by the molecular-orbital method the localisation energy has been calculated[188] as 30 kcal for a bond in benzene, 22 kcal for the 1–2 bond in naphthalene, and 37 kcal for the 2–3 bond. The considerably lower localisation energy explains why naphthalene reacts at the 1–2 bond. The localisation

energy of the 9–10 bond in the phenanthrene molecule is still lower, amounting to only 16 kcal, etc. There is no doubt that the magnitude of the localisation energy is one of the most important factors governing the reactivity of an aromatic bond. In a study of the ozonisation reaction, for example, it was established that, if the difference in localisation energy of two bonds is taken as equivalent to the difference in activation energy, the calculated difference in reaction velocity is in good agreement with the experimental value. At the same time, as Brown[188] has shown, the localisation energy of a bond is very clearly connected with the bond order (see Fig. 2. in Brown[188]). The relationship between the energy and the length of a bond has also been discussed by Pauling[189].

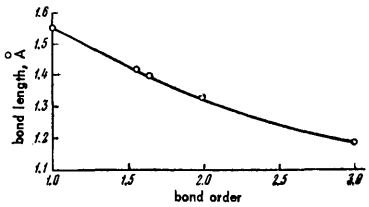


Fig. 1.

The order and the localisation energy of a bond are also closely related to the oxidation–reduction potential of the corresponding *o*-quinone. This fact was first noted as early as 1940 by Clar[190], who pointed out that the more active a hydrocarbon the less reactive is the quinone obtained from it. This question was subsequently discussed in a number of papers[191-193]. The relationship between the order of a bond and the oxidation–reduction potential of the corresponding *o*-quinone is shown by the graph in Fig. 3 [78].

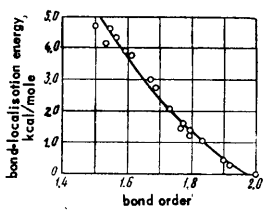


Fig. 2.

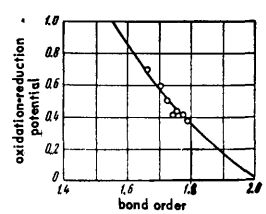
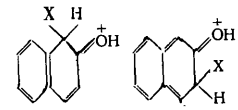


Fig. 3.

This relationship enables the order of the C–C bond of a compound to be found when the oxidation–reduction potential of the corresponding *o*-quinone has been determined. On the other hand, it explains why 2,3-naphthaquinone is so difficult to obtain, and so far has still not been prepared: this quinone should be very unstable, since its oxidation–reduction potential should be considerably higher than the potential of the not very stable *o*-benzoquinone. Finally, the same relationship sheds additional light on the cause of the selective substitution of 2-naphthol at position 1. The formation of an intermediate product of quinonoid structure is obviously of great significance here.



It can be seen that the addition of a cation to position 1 should give a far more stable intermediate than addition to position 3. Thus, for this reason too, when there are two possible *ortho*-positions, attack occurs where the bond order is high.

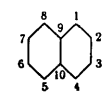
THE EFFECT OF A FUSED RING ON THE BENZENE RING IN CONDENSED SYSTEMS

The chemical and physical data given above and the results of quantum-mechanical calculations show that in the benzene molecule all the bonds are completely equivalent, and the electrons forming them are delocalised, but that in aromatic compounds having condensed rings the C–C bonds are not the same, some of them being more unsaturated and having a higher order (being more "double-bonded") than others. In these cases partial localisation of the double and single bonds is said to occur. As is clear from the above, this partial localisation of bonds has a very great influence, in many cases even a decisive effect, on the chemical behaviour of aromatic compounds, and is therefore of particular interest.

From a comparison of unsubstituted benzene with compounds in which the benzene ring forms part of a fused-ring system, it can be concluded that the partial localisation of the double bonds in the benzene ring of such compounds is due to the influence of the adjacent ring. Such a treatment enables the causes of this influence and the opportunities for exercising it to be examined in an approximate, qualitative fashion.

Examination of the literature shows that only a fused ring of aromatic character has such an effect, independently of whether it is carbocyclic or heterocyclic. The saturated five- and six-membered rings in the indane and tetralin molecules hardly produce any bond fixation in the benzene rings: the Mills–Nixon effect does not exist.

As has been said above, the simplest molecule in which the partial localisation of double bonds can be clearly detected is naphthalene. In this compound the phenomenon is caused by the mutual influence of two condensed benzene rings, each of which requires the π electrons of the adjacent atoms 9 and 10 to form a stable π-electron sextet[194].



A simple explanation of the mechanism of this phenomenon was put forward a few years ago by Shigorin[195]. It is based on the following elementary but completely logical postulates:

1) In a molecule having conjugated bonds (under appropriate conditions) any π electron simultaneously interacts (forms bonds) with all its closest neighbours having π electrons with antiparallel spins.

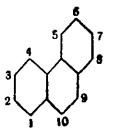
2) The nature of the interaction of π electrons having anti-parallel spins is such that a strengthening (or a weakening) of their interaction with some of their neighbours leads to a weakening (or a strengthening) of their interaction with the others.

3) In the systems under consideration the characteristics of the bonds and the atoms vary linearly with change in the number of neighbours and their electronegativity.

Using these postulates Shigorin[196,197] recently deduced simple equations providing a very easy method of calculating values of the unsaturation, bond orders, interatomic distances, and bond energies which are in very good agreement with those found experimentally or calculated by the molecular-orbital method. A special merit of Shigorin's work in this field is that his equations and the deduction of them follow directly from the peculiarities of the chemical structure of the molecules, and are therefore comprehensible and accessible to the organic chemist.

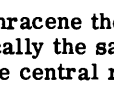
According to Shigorin the breakdown of bond equivalence in the naphthalene molecule is explained by the π electrons of atoms 9 and 10 (common to the two rings), unlike the remaining ones, interacting with three neighbouring π electrons. Because of this, the 9–10, 1–9, 8–9, 4–10, and 5–10 bonds should have a diminished order. The order of the 1–2, 3–4, 5–6, and 7–8 bonds should be correspondingly greater, and that of the 2–3 and 6–7 bonds lower.

These arguments are applicable also to more complicated compounds. Thus examination of the phenanthrene molecule shows that in its outer rings there should be a partial localisation of butadiene groupings, as in the naphthalene rings.



The order of the 1–2, 3–4, 5–6, and 7–8 bonds is increased. In the central ring the ethylene link is partially localised in the 9–10 position. Since this localisation occurs under the simultaneous influence of two benzene rings, the resulting bond order should be considerably greater than that of the 1–2 and 3–4 bonds in the outer rings.

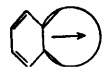
In the molecule of anthracene the state of the bonds in the outer rings is practically the same as in naphthalene and phenanthrene. In the central ring, however, the influence of the two adjacent benzene rings should lead to a partial localisation in positions 9 and 10 of single unpaired π electrons. This leads also to the appearance in the anthracene molecule of the specific high reactivity of the *meso*-positions[198]. Quantum-mechanical calculation, in its turn, confirms this conclusion, indicating the increased free-valency index of the *meso*-positions in anthracene.



These arguments can also be readily used to characterise the state of the bonds of more complex hydrocarbons. The conclusions which are reached are in good qualitative agreement both with the results of calculation and direct determination of interatomic distances and with data from chemical investigations.

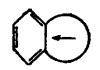
There arises, however, the more general question of the nature of the effect of the heterocyclic or non-benzenoid aromatic ring on the state of the bonds in the condensed benzene ring[198]. In the above cases it was assumed that the π electrons of the shared carbon atoms were equally necessary for the completion of the aromatic sextets of the two condensed rings. In the case of heterocyclic and non-benzenoid aromatic rings this may still be the case, and then the partial localisation of the double and single bonds in the condensed benzene ring should not differ substantially from the localisation occurring in naphthalene. However, if the added ring possesses a considerably greater or considerably smaller affinity for π electrons than that of the benzene ring, there is theoretically the possibility of the existence of two types of partial localisation of double and single bonds in the benzene ring[199].

In the first case it may be expected that the fused ring will "pull" the π electrons of the common carbon atoms out of the benzene ring, leaving in it only a partly localised butadiene grouping similar to that existing in *o*-quinones:



Such a transfer of electrons can obviously be regarded as an intramolecular oxidation–reduction process, in which the benzene ring of the molecule is oxidised with simultaneous reduction of the fused ring[200].

In the second case the fused ring does not require the π electrons of the common atoms for its energetic stability. It either exerts no effect on the state of the bonds in the benzene ring* or, possessing an excess of π electrons, it will "push" the π electrons of the common atoms into the benzene ring, causing a partial localisation of the double and single bonds, similar to that erroneously proposed for indane:



Below we shall examine some experimental results relevant to the existence of these three types of interaction between the benzene and the fused rings in condensed-ring molecules.

Two Condensed Rings Possessing Approximately Equal Affinity for π Electrons

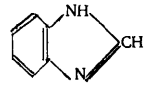
Partial localisation of double and single bonds has been observed in the benzene ring of quinoline (LI) and isoquinoline (LII). This localisation is similar to that occurring in the naphthalene molecule.

(LI) (LII)

* We have already met such cases in tetralin and indane.

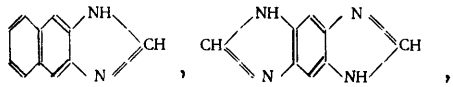
Results have already been given above for ozonisation, transmission of conjugation effect, substitution reactions, and certain other data[201] which confirm such localisation.

Localisation of this type is apparently encountered quite often, being produced under the influence not only of six-membered but also of five-membered heterocyclic rings of aromatic character. A study of such systems was described by Fries and his coworkers[98]. The methods of investigation adopted in their work are identical with those employed for the study of naphthalene. However, the discussion of the results of chemical experiments is complicated in these cases by the necessity for taking account of the influence of the polarity of the hetero atoms on the chemical properties. In the case of benzimidazole (LIII), for example, this leads to the β-position being, in contrast to naphthalene, more reactive than the α-position[202,203].



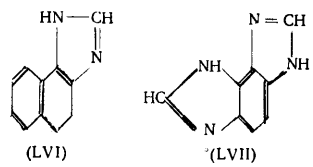
(LIII)

With such heterocyclic compounds, therefore, a valuable method for ascertaining the nature of the mutual influence of the rings is to study the chemical properties of the linear and angular tricyclic molecules. With approximately the same affinity for π electrons in all the rings, the reactivity of the central benzene ring of the compound of linear structure should be similar to the reactivity of anthracene described already, and that for the angular molecule should correspond to phenanthrene. Thus the properties of 2,3-naphthimidazole[105] (LIV) and 1,2:4,5-bisimidazolobenzene (LV)[204],



(LIV) (LV)

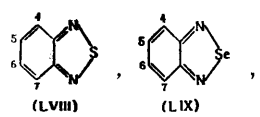
are very like those of anthracene, but the behaviour of 1,2-naphthimidazole (LVI)[205-207] and 1,2:3,4-bisimidazolobenzene (LVII)[194,208] resemble that of phenanthrene.



(LVI) (LVII)

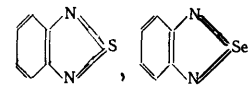
Molecules with a Fused Ring Possessing Considerably Greater Affinity for π Electrons than the Benzene Ring

Benzothiadiazole (LVIII) and benzoselenadiazole (LIX)[199],



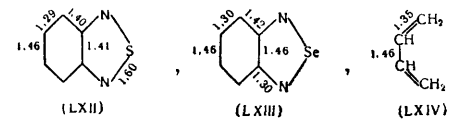
(LVIII) (LIX)

are examples of compounds in which a strongly electrophilic heterocyclic ring causes a marked disturbance to the bond equivalence with formation of a quinonoid structure in a condensed benzene ring. These compounds are obtained by condensation of *o*-phenylenediamine with sulphur dioxide[209,210] (and also thionyl chloride)[211] and with selenium dioxide[209] respectively; from their methods of preparation their structures can be represented as



(LX) (LXI)

However, the presence of cumulative bonds in the ring made the validity of the last two structures doubtful. In 1951 Luzzati[212] determined the interatomic distances in these substances, as shown in LXII and LXIII:

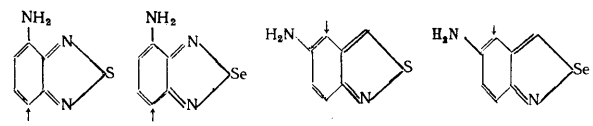


(LXII) (LXIII) (LXIV)

These interatomic distances indicate clearly that the benzene ring has a quinonoid structure. Thus closure of the heterocyclic rings produces in this case a considerable rearrangement of the π electron cloud of the whole molecule: to achieve stability the heterocyclic ring has "extracted" two π electrons from the benzene ring, and has partially localised the butadiene grouping in it. It is also noteworthy that in these molecules the localisation of the bonds in the benzene ring is considerably more marked than in the preceding case: the interatomic distances of the butadiene grouping localised in the benzene ring differ little from those in butadiene itself (LXIV).

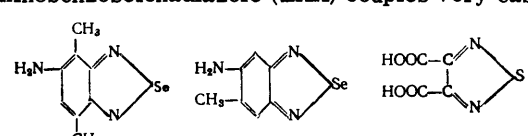
The question arises as to how this affects the chemical properties of these substances. Investigation shows that, as for other aromatic compounds, their most characteristic reactions are of substitution, occurring primarily at the α-positions (positions 4 and 7): nitration[199,200,213,214], sulphonation, and chlorination in the presence of a catalyst[215]. During chlorination and bromination in the absence of a catalyst, as Khaletskii and his coworkers have shown[216,217], benzothiadiazole (LVIII) can add on four atoms of halogen at the butadiene grouping with formation of unsaturated ring products.

The isomeric 4- and 5-amino derivatives of benzothiadiazole and benzoselenadiazole are intensely coloured, possess low basicity ($pK_B \cong 11.3$), and do not differ in chemical properties from ordinary aromatic amines. They give acyl derivatives, are readily diazotised, and undergo the Sandmeyer reaction. These amines readily couple with diazonium compounds, the 4-amino derivatives LXV and LXVI coupling in position 7, but the 5-amino derivatives LXVII and LXVIII solely in position 4.[200,215,218]



(LXV) (LXVI) (LXVII) (LXVIII)

If position 4 is blocked by a methyl group, the resulting substances are no longer able to couple. Thus 4,7-dimethyl-5-aminobenzoselenadiazole (LXIX) does not couple even with very active diazo compounds, whereas 6-methyl-5-aminobenzoselenadiazole (LXX) couples very easily[219].

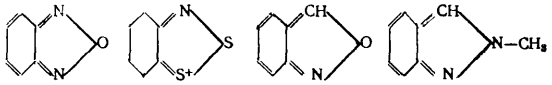


(LXIX) (LXX) (LXXI)

Ozonisation of benzothiadiazole and also oxidation with permanganate occur in the first place at the 4–5 and 6–7 bonds, yielding thiadiazole dicarboxylic acid (LXXI).[220] However, in spite of the large degree of bond fixation, these compounds do not undergo diene-synthesis reactions[200].

The quinonoid character of the benzene rings is shown in the intense colour, the absorption spectra, the addition of halogens already mentioned, and also in the ease with which the heterocyclic rings are opened by reduction in an acid medium[215,218,221].

A number of substances are already known which exhibit an analogous type of dissymmetry of the benzene ring. Among them may be mentioned in particular benzoxadiazole (LXXII)[212], the benzothiazothiolium cation (LXXIII) obtained by the Hertz reaction, and also, judging from spectroscopic data[222], anthranil (LXXIV) and 2-methylindazole (LXXV).

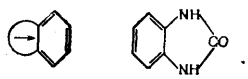


(LXXII) (LXXIII) (LXXIV) (LXXV)

However, the chemical properties of these products have not yet been extensively studied.

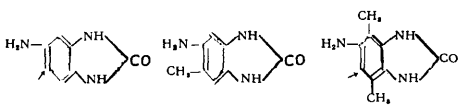
Compounds with a Fused Ring Possessing an Excess of Electrons, which "Expels" the π Electrons of the Common Atoms into the Benzene Ring

As has already been pointed out, an enrichment of the benzene ring with π electrons should theoretically lead to the partial localisation of double bonds shown in LXXVI:

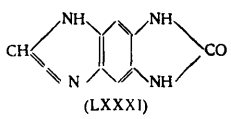


(LXXVI) (LXXVII)

Unfortunately there exist at present only a limited number of chemical data which might be regarded as providing experimental confirmation of the existence of this type of phenomenon. These concern the chemical properties of benzimidazolone (LXXVII) and have been obtained only very recently[223]. In accordance with the partial bond fixation in the benzene ring, 5-aminobenzimidazolone (LXXVIII) very readily undergoes azo coupling, which occurs exclusively at position 6.[224] Blocking of this position with a methyl group leads to 5-amino-6-methylbenzimidazolone (LXXIX), which does not couple, whereas 5-amino-4,7-dimethylbenzimidazolone (LXXX) couples readily with diazonium compounds[225].



(LXXVIII) (LXXIX) (LXXX)



(LXXXI)

Some confirmation of the influence of the imidazolone ring on the benzene ring may be provided also by the fact that 2'-oxo-1,2 : 4,5-bisimidazolobenzene (LXXXI) is not at all like 1,2 : 4,5-bisimidazolobenzene (LV) (already mentioned) or anthracene in chemical properties. The reason for this difference becomes clear if it is accepted that in this case the two heterocyclic rings simultaneously produce in the benzene ring bond fixation as shown in LXXXI, instead of the partial localisation of single π electrons in the *meso*-positions characteristic of anthracene[226].

Such are the experimental data at present available concerning the three possible types of partial localisation of double and single bonds in the benzene ring produced under the influence of a condensed ring. The review shows that the first two types definitely exist, but the existence of the third has not yet been demonstrated beyond doubt.

Further investigations of the mutual influence of cyclic groups in fused-ring molecules and clarification of the nature of the accompanying partial localisation of double and single bonds will enable a fresh approach to be made to the solution of many complicated questions of the chemistry of carbocyclic and heterocyclic aromatic compounds.

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DIENE SYNTHESES WITH NITRO COMPOUNDS

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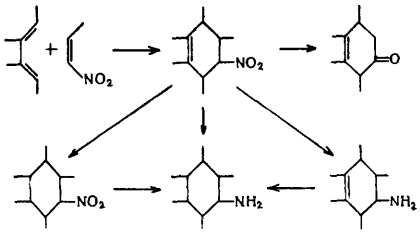
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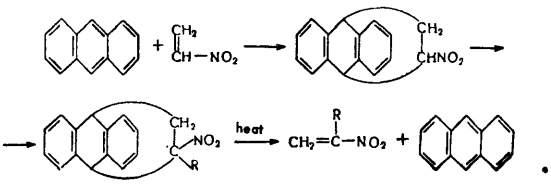
INTRODUCTION

From information available on diene syntheses with nitro compounds, it is evident that the introduction of a nitro group into the molecule of a diene or dienophile considerably changes their reactivity in the Diels–Alder reaction. Nitrophilodienes, containing a nitro group conjugated with a double bond, condense with dienes more readily than ordinary ethylenes. However, a nitro group has an inhibiting effect on the diene system and nitrodienes show reduced reactivity in the Diels–Alder reaction.

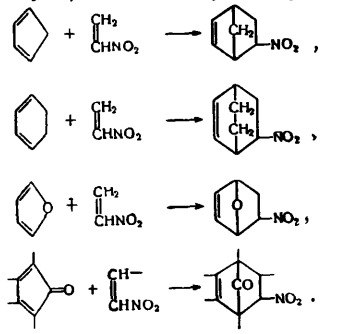
The diene condensation of unsaturated nitro compounds yields adducts with a nitro group and a double bond in the molecule, from which a series of interesting products can be synthesised, which are either unobtainable or obtainable only with difficulty by other methods. By the reduction of nitro-adducts under different conditions and in the presence of different catalysts, saturated alicyclic nitro compounds[1], and unsaturated and saturated amines[1,2] can be obtained. Using the Nef reaction the corresponding ketones[3,4] can be synthesised.



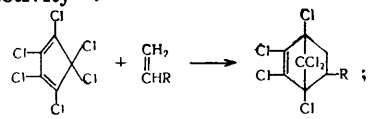
The saturated amines formed in this way can be used as starting materials for the synthesis of polynuclear heterocyclic compounds containing nitrogen[5]. Diene syntheses can be used in the synthesis of α-substituted nitro-olefines[6]:



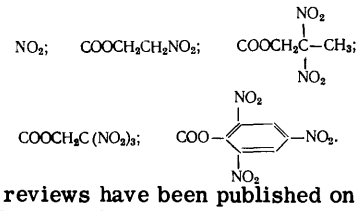
Diene reactions can further be used for preparing bicyclic nitro compounds, containing endomethylene[1,2,3], endoethylene[7], endo-oxy-[8], and carbonyl bridges[9]:



Compounds with insecticidal activity have been prepared by the condensation of *o*- or *m*-nitrostyrenes with hexachlorocyclopentadiene and the subsequent reduction of the nitro groups in the adducts to amino groups[10]. Condensations of hexachlorocyclopentadiene with nitroethylene, and with 2-nitroethyl, 2,2-dinitropropyl, 2,2,2-trinitroethyl, and 2,4,6-trinitrophenyl esters of acrylic acid yield adducts with insecticidal activity[11]:



where



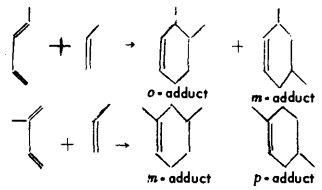
Although many reviews have been published on the diene synthesis, several stereochemical problems remain to be elucidated. Moreover, the chemical properties of the adducts obtained from the unsaturated nitro compounds have not yet been fully discussed. We have therefore dealt with these questions in this review.

Tables at the end of the paper summarise all the material on the diene synthesis of nitrodienes and nitrophilodienes, published up to the beginning of 1959.

THE MECHANISM OF THE DIELS–ALDER REACTION

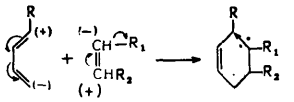
Despite a substantial volume of experimental data on diene reactions and several important theoretical generalisations on the stereochemistry of the products, there is at present no general agreement on the reaction mechanism[12–16].

When asymmetrical addends are used, the question of the mutual orientation of the diene and the philodiene arises. If a 1- or 2-substituted diene and a monosubstituted olefine are used, in each case two structurally different adducts can be formed, e.g.:

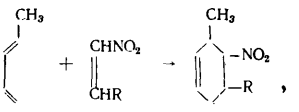


Since the condensation of dienes $CH_2=CH-CH=CHR$ (where

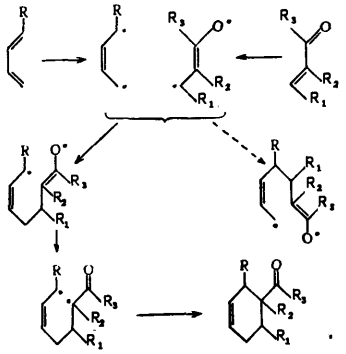
R = alkyl, *O*-alkyl, aryl) with philodienes $R_2CH=CHR_3$ (where R_2 = COOH, COOalkyl, CHO, $C\equiv N$, NO_2 . . . . , and R_3 = H, alkyl, aryl) in most cases yielded only the *o*-adduct, and the condensation of dienes $CH_2=CR_1-CH=CH_2$ with philodienes $R_2CH=CHR_3$ yielded mainly the *p*-adduct, an ionic reaction mechanism was suggested for the diene synthesis. In this mechanism, the anionoid end of the diene system adds to the cationoid end of the dienophile, forming a bipolar ion, which quickly cyclises to the adduct[17-21]:



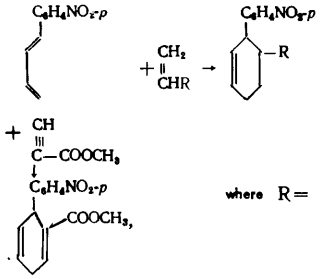
This hypothesis is fully consistent with the experimental data of Kataev and Matveeva, who by condensation of piperylene with 1-nitro-olefines of the type $NO_2CH=CHR$, obtained adducts in which the methyl and the nitro group are in *o*-position to each other[22]:



where R = $CH_2CH_2CH_3$, C_6H_5, and 2-furyl. According to this mechanism, the reaction of dienes containing an electronegative substituent in position 1 with philodienes also containing an electronegative substituent, should yield the adducts in which the electronegative substituents are *meta* to each other. However, in practice the *o*- and *p*-isomers are formed. This paradox may, according to some authors, be explained by assuming the diene synthesis to proceed via a reactive non-cyclised complex, or through the formation of a biradical intermediate and its subsequent cyclisation. Kataev[21], using the data of Alder, Schumacher, and Wolf[23], and also of Snyder and Poss[24], has suggested the following reaction path for the diene synthesis:



Kataev's scheme is consistent with the reaction of 1-(*p*-nitrophenyl)-1,3-butadiene with acrylic acid, acrylonitrile, and methyl propiolate to yield *o*-adducts, whereas by the ionic mechanism the *m*-adducts should be formed.

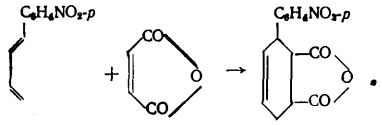


where R= COOH, CN .

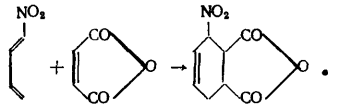
Most workers would now agree that the diene synthesis proceeds through an intermediate cyclic complex. In considering the direction of the reaction and the mutual orientation of the diene and the dienophile, one should remember that in the initial stage the electrostatic factors are of secondary importance, and that the conjugation in the intermediate stage plays a more important role. The presence of substituents may change the difference between the conjugation energy of the active complex and the initial stage, and this may manifest itself in the activation energy[25].

DIENE SYNTHESIS WITH NITRODIENES

Kataev, in his work, drew attention to the small reactivity of 1-(*p*-nitrophenyl)-1,3-butadiene. The yields of the corresponding adducts were usually in the 25–30% range; only with such an active philodiene as maleic anhydride did the yield reach 70%:[21]

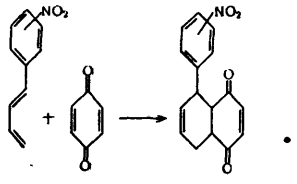


To elucidate more completely the effect of the nitro group on the diene synthesis, Kataev[21] studied the condensation of 1-nitrobutadiene with maleic anhydride, *p*-benzoquinone, acrolein, acrylonitrile, and dimethyl acetylene dicarboxylate. 1-Nitrobutadiene reacted only with maleic anhydride, giving merely 4% of the adduct.



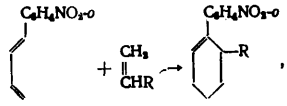
On the basis of these experimental data, Kataev[21] concluded that the α,β-double bond in 1-nitro-1,3-butadiene is considerably inactivated, and that the inactivating effect of the nitro group is diminished by the introduction of a benzene ring between it and the diene system, as in 1-(*p*-nitrophenyl)-1,3-butadiene.

Reactions of 1-(*o*-nitrophenyl)-, 1-(*m*-nitrophenyl)-, and 1-(*p*-nitrophenyl)-1,3-butadienes with *p*-benzoquinone were carried out by Goldberg and Scott[26]:



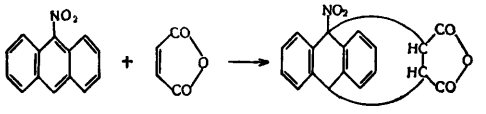
The adducts obtained can be used as amoebocides and fungicides.

1-(*o*-Nitrophenyl)-1,3-butadiene condenses with maleic anhydride, acrolein, and acrylic acid giving the corresponding adducts; the last two philodienes yield adducts with adjacent substituents[27]:

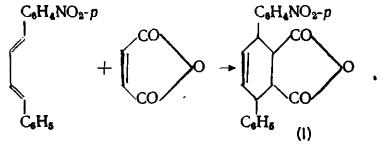


where R = CHO; COOH.

The introduction of a nitro group into the 9-position also has an inhibiting effect on the diene synthesis of anthracene with maleic anhydride. Whereas anthracene itself reacts within 10 min on boiling with maleic anhydride in xylene, giving the adduct in quantitative yield[28], the adduct of 9--nitroanthracene and maleic anhydride is formed in 56% yield by boiling the components for 2 h in xylene[29]:



1-(*p*-Nitrophenyl)-4-phenyl-1,3-butadiene reacts with maleic anhydride when heated in the absence of solvent at 100°, giving the adduct (I) in quantitative yield[30]:

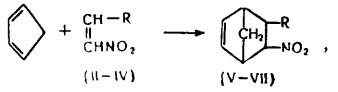


(I)

DIENE SYNTHESIS WITH NITROPHILODIENES

The presence in the philodiene of a nitro group conjugated with the double bond facilitates the diene synthesis, although the presence of a nitro group in the diene acts as an inhibitor, as shown above. The following unsaturated nitro compounds as philodienes in the Diels–Alder reaction have been used: nitroethylene and its homologues and derivatives, β-nitrostyrene and its homologues and derivatives, and 1,1-dinitroethylene.

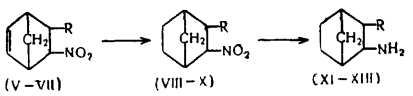
The condensation of nitro-olefines (nitroethylene, nitropropylene, and nitroamylene) with cyclopentadiene was first carried out by Alder and his collaborators. They showed, with nitroethylene as an example, that the condensation proceeded according to diene synthesis[1]:



(II–IV) (V–VII)

where R = H (II), R = CH_3 (III), R = C_3H_7 (IV), R = H(V), R = CH_3 (VI), and R = C_3H_7 (VII).

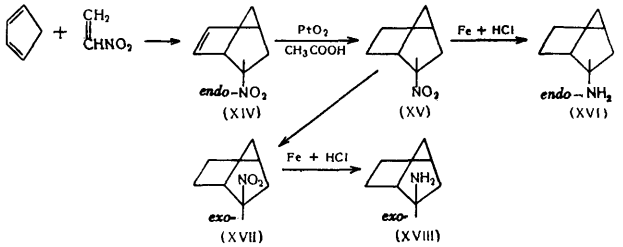
The structure of the adducts obtained was determined by transforming them into known products. The nitro-adducts (V), (VI), and (VII) were hydrogenated over platinum oxide to form the saturated nitro compounds (VIII), IX), and (X), which could be reduced by zinc or iron powder and hydrochloric acid to saturated amines (XI), (XII), and (XIII):



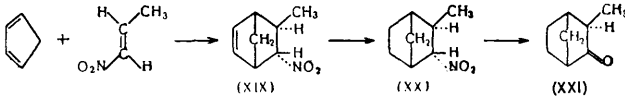
(V–VII) (VIII–X) (XI–XIII)

Amine (XI), prepared from nitro-adduct (V), was identical with *endo*-norbornylamine, already described in the literature. Similarly, (VIII) was identical with 2-nitronorcamphane, and (V) with 5-nitronorbornylene. These results indicated that the reaction of nitroethylene with cyclopentadiene proceeded with 1,4-addition. Adduct (V) showed that the diene synthesis with nitro-olefines followed the rule of the maximum accumulation of double bonds, formulated by Alder, and that the nitro-adduct had the *endo*-configuration.

Later work by Roberts, Lee, and Saunders[31] confirmed the stereospecific effect of the nitro group on the diene synthesis. In their opinion[31], the condensation of nitroethylene with cyclopentadiene yielded 90% of the adduct with the *endo*-configuration (XIV). They arrived at this conclusion because hydrogenation of adduct (XIV) gave *endo*-2--nitronorcamphane (XV), which was subsequently reduced to *endo*-norbornylamine (XVI). Isomerisation (heating with triethylamine) of *endo*-2-nitronorcamphane gave *exo*-2--nitronorcamphane (XVII), which was reduced to *exo*-norbornylamine (XVIII)[31].

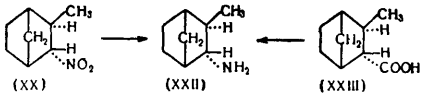


To establish the steric configuration of the substituents in the reaction product of nitropropylene and cyclopentadiene, van Tamelen and Thiede[32] carried out the selective hydrogenation of the nitro-adduct (XIX) over platinum oxide to (XX), and subsequently obtained the ketone (XXI) by the Nef reaction. Ketone (XXI) was shown to be identical with 3--*exo*-methylbicyclo[2,2,2]heptanone, already known:



(XIX) (XX) (XXI)

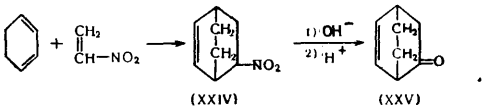
For conclusive confirmation of the *exo*-configuration of the methyl group, the nitro-adduct (XX) was reduced by means of iron and acetic acid to the amine (XXII):



(XX) (XXII) (XXIII)

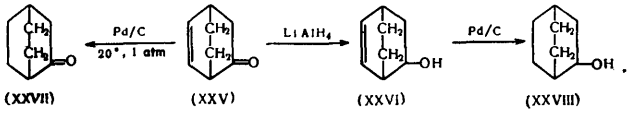
Amine (XXII) proved to be identical with the amine obtained by the Schmidt reaction from 2-*endo*-carboxy-3-*exo*-methylbicyclo[1,2,2]heptane (XXIII), whose configuration was known with certainty[32].

Wildman and Saunders observed the interesting case of the formation of an *endo*-ethylene bridge (XXIV) on boiling a mixture of nitroethylene and cyclo-1,3-hexadiene:[7]



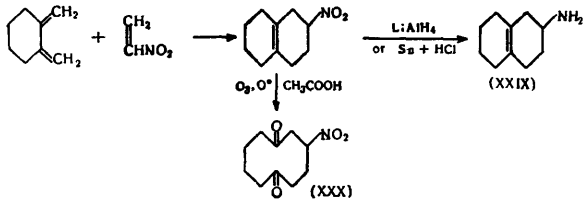
(XXIV) (XXV)

The adduct was subsequently subjected to the Nef reaction, the unsaturated ketone (XXV) thus formed was transformed into the unsaturated alcohol (XXVI). The ketone and alcohol were hydrogenated to the saturated compounds (XXVII) and (XXVIII)[7]:

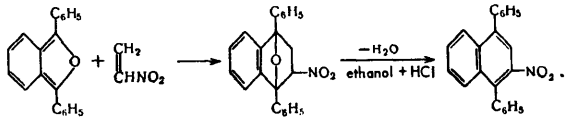


(XXVII) (XXV) (XXVI) (XXVIII)

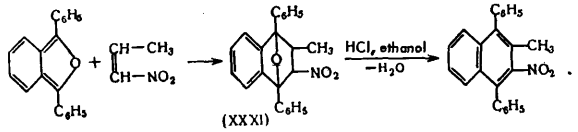
The reaction of nitroethylene with 1,2-dimethylenecyclohexane is highly exothermic, and yields 85% of 2-nitro--1,2,3,4,5,6,7,8-octahydronaphthalene, which can be reduced by $LiAlH_4$ or Sn + HCl to the unsaturated amine (XXIX), or oxidised by ozone to 3-nitrocyclodecane-1,6-dione (XXX)[33].



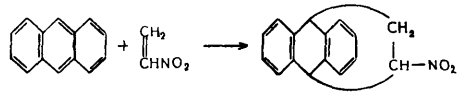
Nitroethylene reacts exothermically with 1,3-diphenylisobenzofuran giving quantitatively an adduct which, on dehydration with ethanol-HCl, is transformed into 1,4-diphenyl-2-nitronaphthalene[8]:



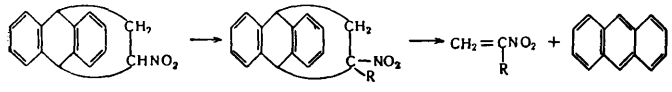
The reaction of 1-nitro-1-propene with 1,3-diphenylisobenzofuran yields two stereoisomeric adducts (XXXI), b.p. 188°–189° and 157°. Only the higher-boiling isomer eliminates water in the presence of ethanol-HCl to form an aromatic compound[8]:



Klager condensed nitroethylene with anthracene by heating them in *o*-dichlorobenzene solution at 145°–150° for 45 min:

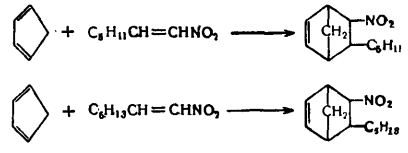


The adduct obtained was used for synthesising nitro-olefines[6]:

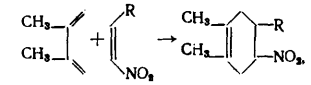


where R = CH_2OCOCH_3, $CH_2CH_2OCOCH_3$, CH_2CH_2CN.

The nature of the nitro-olefine has a considerable effect on the course of the diene synthesis. For instance, nitroethylene adds to cyclopentadiene at room temperature (67% yield)[3], whereas its homologues 1-nitroheptene and 1-nitrooctene condense with cyclopentadiene only at 100°:[34]

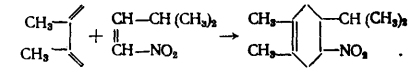


According to Drake and Ross[35], 2,3-dimethyl-1,3-butadiene condenses equally easily with all nitro-olefines, irrespective of their molecular weight:

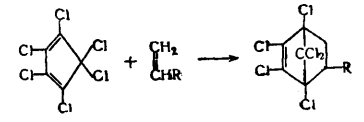


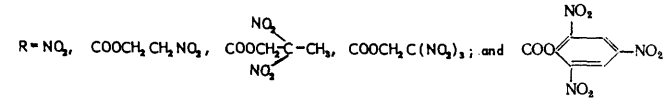
where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9, C_5H_{11}, C_6H_{13}.

However, if there is a bulky group (R = iso-C_3H_7) near the double bond of the nitro-olefine, condensation with 2,3--dimethyl-1,3-butadiene is considerably hindered and the yield of the adduct, under comparable conditions, is decreased[35]:



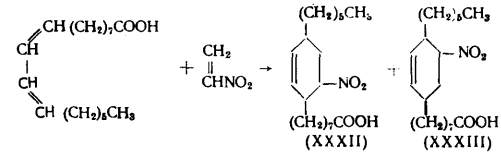
In some cases the steric hindrance is so pronounced that the diene synthesis is practically impossible. An example is encountered in the condensations of hexachlorocyclopentadiene with unsaturated nitro compounds of the structure $CH_2=CHR$ (where R = NO_2, $COOR'NO_2$) and $NO_2CH=CHR''$ (where R'' = alkyl, aryl, $COOCH_3$ and CN). The nitro-olefines of the latter type do not form adducts even when the components are heated above 100° for 20–30 h.[11] However, hexachlorocyclopentadiene condenses with nitrophilodienes of the type $CH_2=CHR$, giving the corresponding adducts in good yields[11]. Cyclopentadiene, as mentioned above, reacts quite easily with nitro-olefines $CH(NO_2)=CHR$ (where R = alkyl, aryl).





The steric hindrance, which has such a powerful effect on the condensation of hexachlorocyclopentadiene with nitrophilodienes $NO_2CH=CHR''$, apparently depends on two main factors. Firstly, the *trans*-position of the substituents in nitrophilodiene[32] probably inhibits the condensation with dienes, since the diene synthesis is considered to be exclusively a *cis*-addition. Secondly, the bulky chlorine atoms in the 5-position of hexachlorocyclopentadiene, hinders condensation with philodienes[36].

The condensation of nitroethylene with dienes containing different alkyl substituents in positions 1 and 4 is expected to form two stereoisomeric adducts. From the condensation of nitroethylene with 9,11-octadecadien-1-oic acid (the effect of COOH is negligible), it was possible to isolate the *meta*- and *ortho*-isomers[37] (XXXII) and (XXXIII).



One isomer, m.p. 85°–90°, was isolated in 16.2% yield, the other (a liquid, $n_D^{30°}$ = 1.4870) in 25.2% yield. The

authors did not ascribe structural formulae to the corresponding isomers.

The reaction of nitro-olefines with dienes is limited by their relative activity in the diene synthesis and by their ability to polymerise. 2-Nitro-1-alkenes, e.g. 2-nitro--1-propylene, are less reactive than 1-nitro-olefines. The former type react with cyclopentadiene only upon heating for several hours at 100°, and require careful preliminary purification and the presence of polymerisation inhibitors. Yields of the corresponding adducts are not large (30--40%)[38].

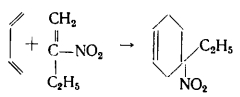


Study of the condensations of 2-nitro-1-butene with cyclopentadiene, butadiene, and 2,3-dimethylbutadiene[39] showed that reaction occurred more easily with the cyclic diene than with the acyclic ones, whereas 1-nitro-1-pentene condensed with both types of dienes with equal ease, and gave good yields of adducts[1].

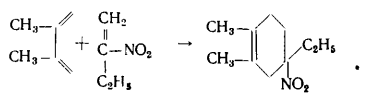
The condensation of 2-nitro-1-butene with cyclopentadiene in an autoclave, at 100°–115°, in the presence of hydroquinone, gave a 61% yield after 3 h[39]:



The adduct from butadiene and 2-nitro-1-butene formed in 37% yield after heating the mixture of components in an autoclave for 4 h at 120°–130°:[39]

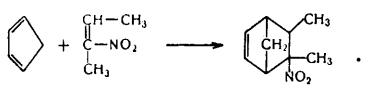


The reaction of 2-nitro-1-butene with 2,3-dimethylbutadiene proceeded more quickly than that with butadiene (under the same conditions it took 2 h). The yield of the product was 40%.[39]

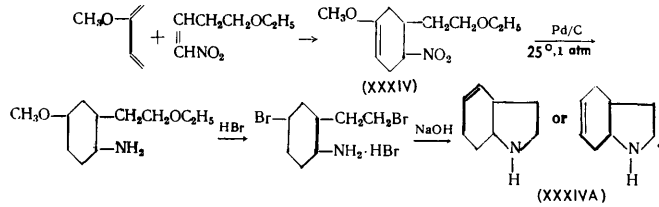


Nightingale and Janes[40] were unable to condense 2--nitro-2-alkenes (2-nitro-4-ethyl-2-hexene, 2-nitro-4--ethyl-2-pentene, and 3-nitro-3-hexene) with cyclopentadiene.

However, others authors later managed[38] to condense 2-nitro-2-butene with cyclopentadiene. The reaction proceeded (~100°) for 5 h and the yield of the nitro-adduct was 41%:



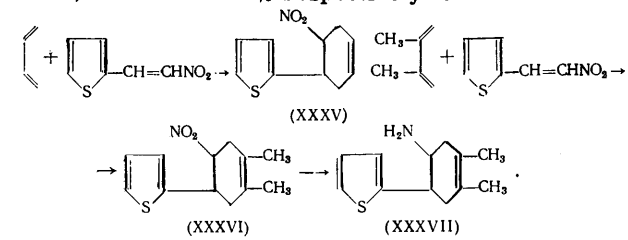
Drake and Ross[5] studied the condensation of 2-methoxy--1,3-butadiene with 4-ethoxy-1-nitro-1-butene and used the adduct obtained (XXXIV) for the synthesis of hexahydroindole (XXXIVA).



(XXXIV)

(XXXIVA)

2-(α-Thienyl)-1-nitroethylene condensed with butadiene and 2,3-dimethylbutadiene under the same conditions (140°, in autoclave, 6 h); the yields of the adducts (XXXV) and (XXXVI) were 61 and 84% respectively[39]:

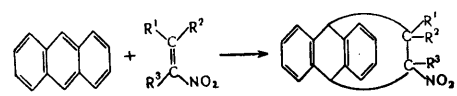


(XXXV)

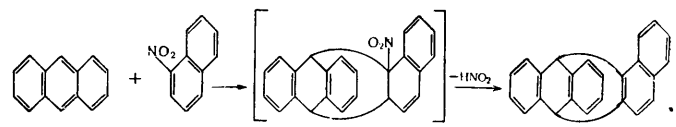
(XXXVI) (XXXVII)

The latter nitro-adduct can be reduced by means of $LiAlH_4$ to unsaturated amine (XXXVII).

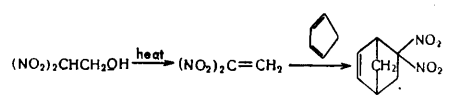
In condensations of anthracene with nitro-olefines of the types $RCH=CHNO_2$ (R = H, CH_3), $CH_2=C(R)NO_2$ (R = CH_3), $RCH=C(R)NO_2$ (R = CH_3), and $RRC=CHNO_2$ (R = CH_3), nitro-olefines of the last two types react with much the greater difficulty[41]:



Hurd and Juel[42] condensed anthracene with 1-nitronaphthalene at 300°, and obtained the adduct which, under the reaction conditions, split off a molecule of nitrous acid and was transformed into a benzotriptycene:



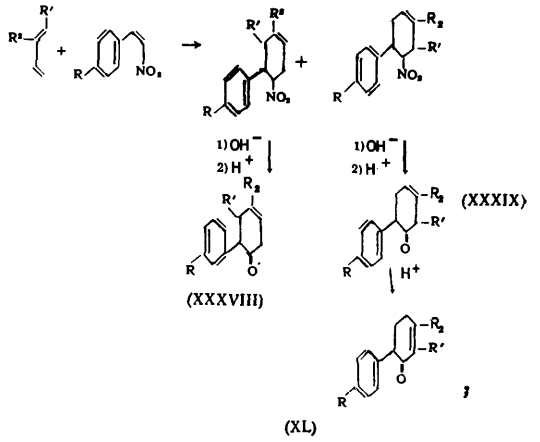
The interesting case of the formation of a *gem*-dinitro-adduct was described by Gold, Hamel, and Klager[43]. Heating cyclopentadiene with 2,2-dinitroethanol in chlorobenzene gave 1,1-dinitrobicyclo[2,2,1]-3-heptene. The authors correctly concluded that under the reaction conditions dinitroethanol is dehydrated to 1,1-dinitroethylene, which condenses with cyclopentadiene:



The behaviour of β-nitrostyrene and its homologues and derivatives in the diene synthesis has been studied very thoroughly. Condensations have been effected with butadiene, 2-ethoxybutadiene, piperylene, isoprene, 1,4-dimethylbutadiene, 2,3-dimethylbutadiene, 2,3-diphenylbutadiene, 1,4-diphenylbutadiene, cyclopentadiene, 3,4-diphenyl-2,5-dimethyl-2,4-cyclopentadien-1-one, 2,3,4,5--tetraphenyl-2,4-cyclopentadien-1-one, cyclohexadiene, phellandrene, 2-vinylcyclohexene, bicyclohexenyl, methyleneanthrone, anthracene, 1,3-diphenylisobenzofuran,

1,3-diphenyl-5,6-dimethylisobenzofuran. β-Nitrostyrene did not react with furan, silvan, and 2,5-dimethylfuran[4,41,44-53].

Butadienes which are substituted in positions 1 and 2 condense with β-nitrostyrene or its derivatives to give two isomers (except in the case of 2-ethoxybutadiene, which only yields one)[4]:



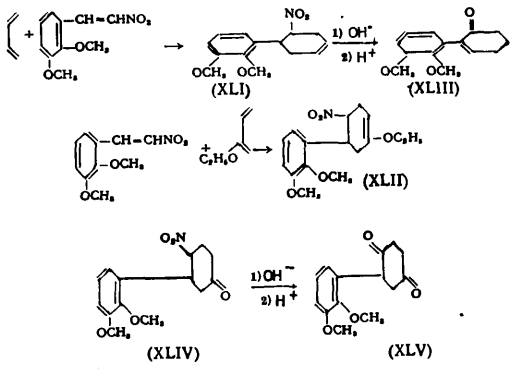
(XXXVIII) (XXXIX) (XL)

a) R = R' = H, $R_2 = OC_2H_5$; b) R = R' = H, $R_2 = CH_3$; c) R = OCH_3, R' = H, $R_2 = CH_3$; d) R = R_2 = H, R' = CH_3.

In reactions with isoprene and piperylene, a mixture of isomers is formed. In cases b) and d), namely in condensations of isoprene (b) and piperylene (d) with β-nitrostyrene, the relative quantities of isomers were determined from the quantities of ketones (XXXVIII) and (XXXIX) formed from them by the Nef reaction. Ketone (XXXIX) is isomerised under the action of acids into the conjugated ketone (XL).

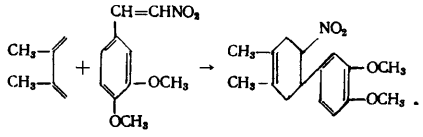
Condensation of butadiene with β-nitrostyrene, and its derivatives (*m*-methoxy-, *p*-methoxy-, and 2,3-dimethoxy-β-nitrostyrene) in toluene at 100° for 48 h, gave adducts in 82–100% yield (see Table 3).[45]

Barltrop and Nicholson[47], in their study of the preparation of intermediate compounds for the synthesis of the morphine series, condensed 2,3-dimethoxy-β-nitrostyrene with butadiene and 2-ethoxybutadiene at 200° for 15 h, using xylene as solvent. They subjected the resulting adducts (XLI) and (XLII) to a series of transformations in order to obtain the corresponding ketones (XLIII), (XLIV), and (XLV):

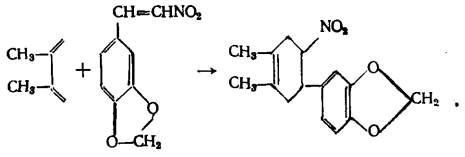


(XLI) (XLIII) (XLII) (XLIV) (XLV)

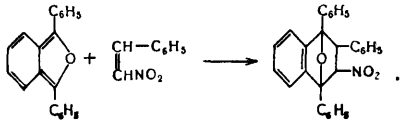
In 1939, 2,3-dimethylbutadiene was condensed with 3,4-dimethoxy-β-nitrostyrene by heating in xylene in a sealed tube at 175°–180° for 10 h[48]; 80% of the adduct was obtained.



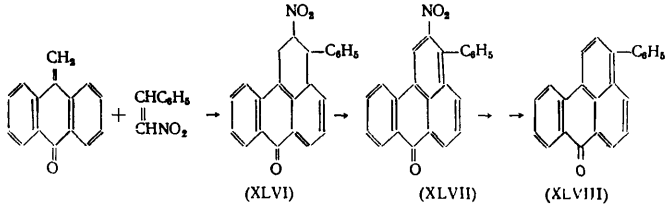
3,4-Methylenedioxy-β-nitrostyrene condenses with 2,3-dimethylbutadiene under the same conditions, yielding 70% of the corresponding adduct[48]:



β-Nitrostyrene gives a quantitative yield of adduct when reacted with 1,3-diphenylisobenzofuran in boiling ethanol for 3 h[46]:

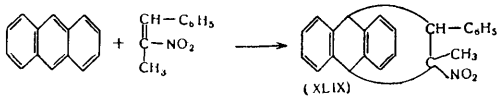


The addition of β-nitrostyrene to methyleneanthrone opened the way to the preparation of poly-condensed systems. The adduct thus formed, (XLVI), was dehydrogenated to form the polycyclic compound (XLVII), the nitro group of which was successively reduced and diazotised using butylnitrite and acetic acid. The diazo group was then replaced by hydrogen by decomposing the diazo compound with ethanol. Compound XLVIII was thus obtained[44,46].



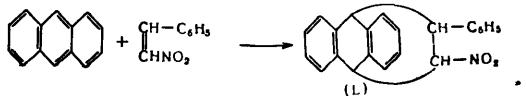
(XLVI) (XLVII) (XLVIII)

By boiling β-methyl-β-nitrostyrene and anthracene in *o*-dichlorobenzene, a low yield (1.4%) of the corresponding adduct (XLIX)[41] was obtained:



(XLIX)

However, β-nitrostyrene condenses with anthracene to give the adduct (L) in good yield[41]:



(L)

The sharp decrease in the yield of adduct (XLIX) as compared with that of adduct (L) can probably be accounted for by steric hindrance.

TABLE 1. Diene synthesis with nitrodienes.

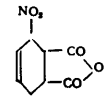
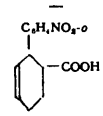
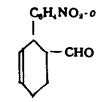
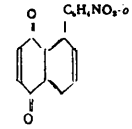
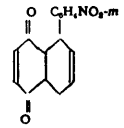
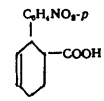
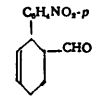
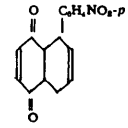
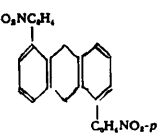
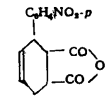
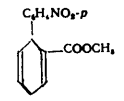
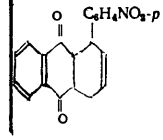
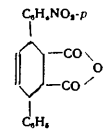
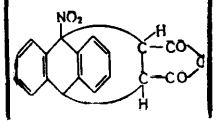
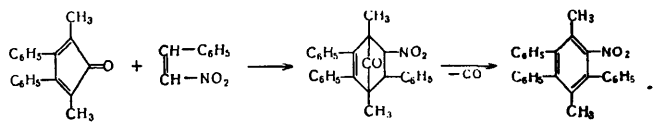
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield, %	Reference
1-Nitro-1,3-butadiene	Acrylonitrile	—	90°—100°	—	0	21
1-Nitro-1,3-butadiene	Acrolein	—	90°—100°	—	0	21
1-Nitro-1,3-butadiene	Benzoquinone	—	90°—100°	—	0	21
1-Nitro-1,3-butadiene	Dimethyl acetylene dicarboxylate	—	90°—100°	—	0	21
1-Nitro-1,3-butadiene	Maleic anhydride		90°—100°	—	4	21
1-Nitro-1,3-butadiene	Naphthoquinone	—	90°—100°	—	0	21
1-(*o*-Nitrophenyl)-1,3-butadiene	Acrylic acid		refluxing for 18 h	m. p. 141°	78	27
1-(*o*-Nitrophenyl)-1,3-butadiene	Acrolein		refluxing for 5 h	m. p. 46° b. p. 100°/10 mm Hg	55	27
1-(*o*-Nitrophenyl)-1,3-butadiene	*p*-Benzoquinone		48 h in acetone without heating	m. p. 93°—97°	—	26
1-(*o*-Nitrophenyl)-1,3-butadiene	Maleic anhydride		15 min at 80° in benzene	m. p. 215°	quant.	27
1-(*m*-Nitrophenyl)-1,3-butadiene	*p*-Benzoquinone		48 h in acetone without heating	m. p. 120°—124°	—	26
1-(*p*-Nitrophenyl)-1,3-butadiene	Acrylic acid		refluxing for 2 h in xylene under nitrogen	m. p. 111°—114°	25—35 71	21 55
1-(*p*-Nitrophenyl)-1,3-butadiene	Acrolein		—	—	25—35	21
1-(*p*-Nitrophenyl)-1,3-butadiene	*p*-Benzoquinone		48 h in acetone without heating	m. p. 170°—174°	16	21 26
1-(*p*-Nitrophenyl)-1,3-butadiene	1,4-Dioxo-5-(*p*-nitrophenyl)-1,4,4',5,8,8'-hexahydronaphthalene		—	—	8	21
1-(*p*-Nitrophenyl)-1,3-butadiene	Maleic anhydride		15 min, 70°	m. p. 170.9°—172°	70	21 56
1-(*p*-Nitrophenyl)-1,3-butadiene	Methyl propiolate		—	—	25—35	21
1-(*p*-Nitrophenyl)-1,3-butadiene	Naphthoquinone		—	—	40	21

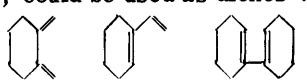
TABLE 1. contd.

Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield, %	Reference
1-(*p*-Nitrophenyl)-4-phenyl-1,3-butadiene	Maleic anhydride		2 h, 100°	—	quant.	30
9-Nitroanthracene	Maleic anhydride		refluxing in xylene for 2 h	m. p. 244°–245°	56	29

To obtain polysubstituted phenylbenzenes, β-nitrostyrene was condensed with 3,4-diphenyl-2,5-dimethylcyclopentan-1-one:[9]

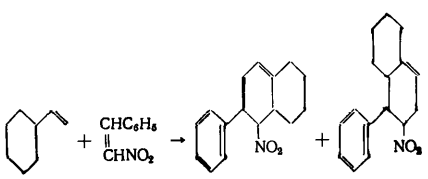


Alder showed that alicyclic compounds with both double bonds semicyclic (LI), as well as vinylcyclenes (LII) and bicyclenes (LIII), could be used as dienes[1]:



(LI) (LII) (LIII)

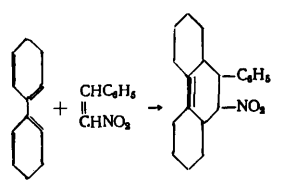
In the condensation of vinylcyclohexene with β-nitrostyrene, the formation of two structural isomers (LIV) and (LV)[48] is possible:



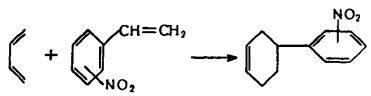
(LIV) (LV)

In the opinion of the authors, the formation of the first one is more probable[48].

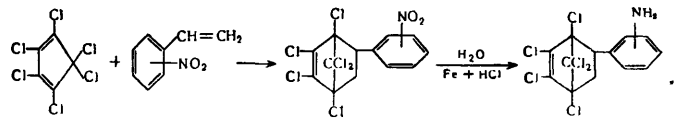
Bergmann and his collaborators[49] condensed β-nitrostyrene with bicyclohexenyl, obtaining 95% of the expected reaction product:



Other nitro-olefines studied were the isomeric *o*-, *m*-, and *p*-nitrostyrenes, which condensed with butadiene to form 44–60% of the corresponding adducts[50]:

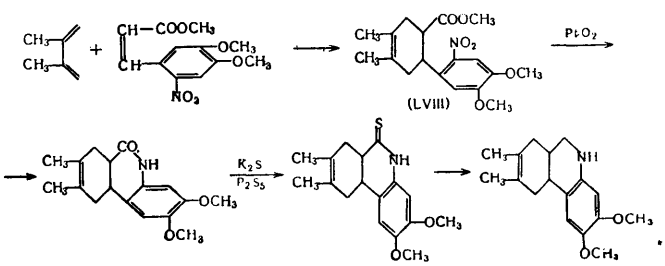


According to an American patent[10], the nitro-adducts (LVI), obtained from *o*- or *m*-nitrostyrenes and hexachlorocyclopentadiene, on reduction yield unsaturated amines (LVII), which possess fungicidal properties:



(LVI) (LVII)

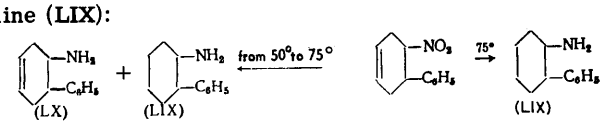
Sugasawa, Kodama, and Hara[51] condensed 2,3-dimethylbutadiene with methyl 3,4-dimethoxy-6-nitrocinnamate, obtained adduct (LVIII), and studied its transformations:



METHODS FOR HYDROGENATION AND REDUCTION OF ADDUCTS

The adducts formed in the condensation of nitro-olefines with dienes contain a nitro group and a double bond. Therefore hydrogenation can lead to three different products, i.e. the saturated nitro compound, and the unsaturated and saturated amines. As the synthesis of these products is very important in determining the configuration of the adducts, we thought it necessary to include in this survey the methods for their selective hydrogenation.

It has been shown for a number of cases[52], that in hydrogenations over Raney nickel catalysts, NO_2 groups are reduced to amino groups at a lower temperature than that required for saturation of the double bond. For instance, the adduct obtained from butadiene and β-nitrostyrene was hydrogenated at 200 atm at 50°–75°. The analysis of the hydrogenation products showed that under these conditions a mixture of the saturated (LIX) and the unsaturated (LX) amines was formed, whereas at 75° the nitro-adduct was completely transformed into the saturated amine (LIX):



(LX) (LIX) (LIX)

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TABLE 2. Diene synthesis with nitrophilodienes, except *p*-nitrostyrene

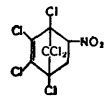
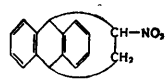
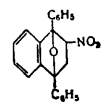
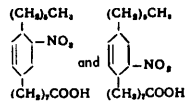
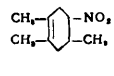
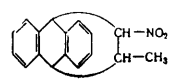
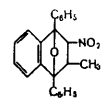
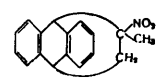
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield %	Reference
Cyclopentadiene	Nitroethylene		8 h in a sealed tube in ether at 105°–100°;	b. p. 70°–90°/15 mm Hg;		1
			8 h in benzene at 18°–20°	92°–94°/8 mm Hg	67	3
Hexachlorocyclopentadiene	Nitroethylene		14 h in chlorobenzene at 100°–102°, in the presence of glacial CH_3COOH	m. p. 160°–161.5°	73	11
1,3-Cyclohexadiene	Nitroethylene		refluxing for 1 h	b. p. 85°–87°/1 mm Hg	33	7
1,2-Dimethylenecyclohexane	Nitroethylene		stirring in cooled ether, then refluxing for 2 h	b. p. 128°–129°/5 mm Hg	85	33
Anthracene	Nitroethylene		8 h in benzene at 110°;	m. p. 113°–114°	76	6
			45 min in *o*-dichlorobenzene at 145°–150°		71	39, 41
1,3-Diphenylisobenzofuran	Nitroethylene		in $CHCl_3$ at 20°	m. p. 178°	99	8
9,11-Octadecadien-1--oic acid	Nitroethylene		heating in benzene in a sealed tube for 48 h	m. p. 85°–90°; liquid isomer $n_D^{20°}$ = 1.4835	16.2 25.2	37
2,3-Dimethyl-1,3--butadiene	1-Nitropropylene		8 h in acetonitrile; without solvent	b. p. 71°/0.6 mm Hg	68.5 72	35
Hexachlorocyclopentadiene	1-Nitropropylene	–	20–30 h at 100°–120°	–	0	11
Cyclopentadiene	1-Nitropropylene		8 h in glacial CH_3COOH at 113°;	b. p. 94°–95°/1 mm Hg;	55	1
			in glacial CH_3COOH at 40°–50°	91.5°–92.5°/11–12 mm Hg	59	32
Anthracene	1-Nitropropylene		in *o*-dichlorobenzene, refluxing for 45 min	m. p. 122.5°–123.5°	62	41
1,3-Diphenylisobenzofuran	1-Nitropropylene	 2 stereoisomers	5 h in $CHCl_3$ at 20°	m. p. 188°–189°, and 157°	41	8
Cyclopentadiene	2-Nitropropylene		in acetic acid at 98°;	m.p. 104°, 84°–86°;	27	38
			90 min in autoclave	b.p. 105°–110°/18 mm Hg	34	39
Hexachlorocyclopentadiene	2-Nitropropylene		20–30 h at 100°–120°	–	0	11
Anthracene	2-Nitropropylene		in benzene in a sealed tube at 110° for 12 h	m.p. 152°–153.5°	19	41

TABLE 2. contd.

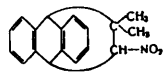
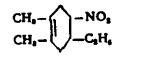
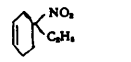
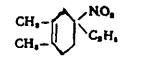
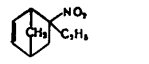
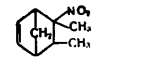
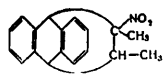
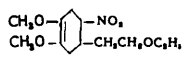
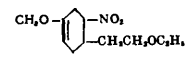
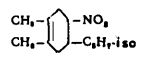
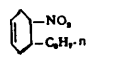
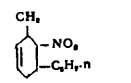
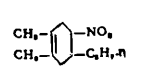
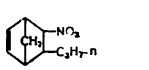
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield %	Reference
Anthracene	2-Methyl-1-nitro-propylene		refluxing in *o*-dichlorobenzene for 4 h	m.p. 147.5–151.5°	0.6	41
2,3-Dimethyl-1,3--butadiene	1-Nitro-1-butene		refluxing in acetonitrile for 16 h	b.p. 105°/4 mm Hg	77.5	35
1,3-Butadiene	2-Nitro-1-butene		4 h in autoclave at 120°–130°	b.p. 82°–84°/5 mm Hg	37	39
2,3-Dimethyl-1,3--butadiene	2-Nitro-1-butene		2 h in autoclave at 140°	b.p. 94°–94.5°/8 mm Hg	40	39
Cyclopentadiene	2-Nitro-1-butene		3 h in autoclave at 103°–115°	b.p. 79°/5 mm Hg	61	39
Cyclopentadiene	2-Nitro-2-butene		5 h, 100°	m.p. 84.5°–86.5°; b.p. 65°/2 mm Hg	41	38
Anthracene	2-Nitro-2-butene		refluxing in *o*-dichlorobenzene for 3.25 h	m.p. 130.5°–132.5°	0.4	41
2,3-Dimethoxy-1,3--butadiene	4-Ethoxy-1-nitro-1--butene		in acetonitrile, refluxing for 34 h; in acetonitrile, refluxing for 40 h	b.p. 112°–114°/1 mm Hg	69	35
2-Methoxy-1,3-butadiene	4-Ethoxy-1-nitro-1--butene		6 h in acetonitrile at 100°	b.p. 137°–138°/2 mm Hg	52–53	5
2,3-Dimethyl-1,3--butadiene	1-Nitro-1-isopentene		in acetonitrile refluxing for 16 h; heating for 16 h at 100°	b.p. 105°/3 mm Hg	31.5 35	35
1,3-Butadiene	1-Nitro-1-pentene		6 h in a sealed tube, at 100°–110°	b.p. 118°/11 mm Hg	–	1
Piperylene	1-Nitro-1-pentene		15 h, 150°	b.p. 108°–110°/6 mm Hg	70	22
2,3-Dimethyl-1,3--butadiene	1-Nitro-1-pentene		6 h in a sealed tube at 100°–110°; 24 h at 100°	b.p. 146°–147°/12 mm Hg; b.p. 113°–114°/5 mm Hg	– 69.5	1 35
Cyclopentadiene	1-Nitro-1-pentene		in benzene, in a sealed tube at 105°–110°	b.p. 122°–125°/1 mm Hg	72	1

TABLE 2. contd.

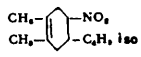
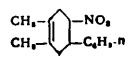
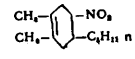
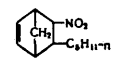
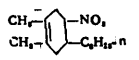
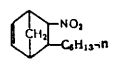
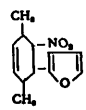
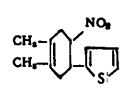
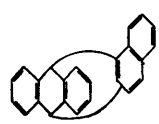
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield, %	Reference
2,3-Dimethyl-1,3--butadiene	1-Nitro-1-isohexene		refluxing in acetonitrile for 32 h; 32 h at 100°	b.p. 115°–116°/3 mm Hg	68.5 65	35
2,3-Dimethyl-1,3--butadiene	1-Nitro-1-hexene		33 h, 100°	b.p. 124°–126°/3 mm Hg	73	35
2,3-Dimethyl-1,3--butadiene	1-Nitro-1-heptene		refluxing for 32 h in acetonitrile	b.p. 129°–130°/3 mm Hg	65	35
Cyclopentadiene	1-Nitro-1-heptene		5 h, 100°	b.p. 122°–123°/5 mm Hg	66	34
2,3-Dimethylbutadiene	1-Nitro-1-octene		24 h, 100°	b.p. 116°/0.3 mm Hg	77–78	35
Cyclopentadiene	1-Nitro-1-octene		4 h, 100°	b.p. 103°/0.5 mm Hg	33	34
Hexachlorocyclo-pentadiene	Methyl nitroacrylate	–	20–30 h, 100°–120°	–	0	11
Hexachlorocyclo-pentadiene	β-Nitroacrylonitrile	–	20–30h, 100°–120°	–	0	11
Piperylene	2-(α-Furyl)nitro-ethylene		8 h at 150°, in a sealed tube	b.p. 120°–122°/4 mm Hg	55	22
1,4-Dimethyl-1,3-butadiene	2-(α-Furyl)nitro-ethylene		16 h at 150° in a sealed tube	b.p. 125°–127°/4 mm Hg	46	22
1,3-Butadiene	2-(α-Thienyl)nitro-ethylene		6 h in autoclave at 140°	m.p. 69°–70°	60	39
2,3-Dimethyl-1,3-butadiene	2-(α-Thienyl)nitro-ethylene		6 h in autoclave at 140°	m.p. 80.5°–81°	60	39
Anthracene	1-Nitronaphthalene		heating for 15 h at 300°	m.p. 207°–208°	44	42
Cyclopentadiene	1,1-Dinitroethylene		30 min in chlorobenzene at 100°–110°	m.p. 117°–118°	–	43

TABLE 2. contd.

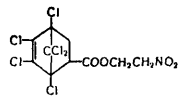
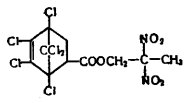
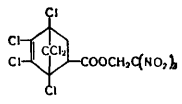
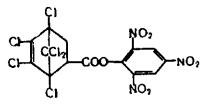
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield %	Reference
Hexachlorocyclo-pentadiene	2-Nitroethyl acrylate		refluxing in chlorobenzene for 21 h	m.p. 93°–94°	89	11
Hexachlorocyclo-pentadiene	2,2-Dinitropropyl acrylate		10 h, 100°–110°	m.p. 114°–115°	quant.	11
Hexachlorocyclo-pentadiene	2,2,2-Trinitroethyl acrylate		refluxing for 20 h in chloro-benzene	m.p. 55°–51°	72	11
Hexachlorocyclo-pentadiene	2,4,6-Trinitrophenyl acrylate		28 h, 100°–110°	m.p. 116.5°–117.5°	65	11

TABLE 3. Diene synthesis with β-nitrostyrene, its homologues and derivatives.

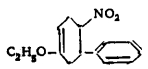
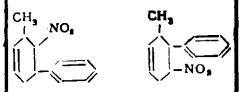
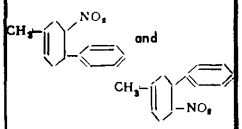
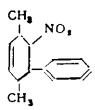
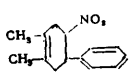
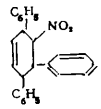
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield, %	Reference
1,3-Butadiene	β-Nitrostyrene		48 h in toluene at 100°; 5 h in toluene at 150°	m.p. 103°	70	46
2-Ethoxy-1,3-butadiene	β-Nitrostyrene		refluxing for 3 h	m.p. 96.5°–97°	66	4
Piperylene	β-Nitrostyrene		10 h, 150°	m.p. 94°–95° and 98°–99°; m.p. 80°–82°	90 87	4 22
Isoprene	β-Nitrostyrene		in toluene at 100°	m.p. of the mixture of isomers 53.5°–54.5°; m.p. 52°	86 7 58	4 44 46
1,4-Dimethyl-1,3-butadiene	β-Nitrostyrene		16 h, 155°	b.p. 149°–151°/4 mm Hg	83	22
2,3-Dimethyl-1,3-butadiene	β-Nitrostyrene		24 h in toluene at 110° 2 h refluxing at 100°	m.p. 96°; m.p. 95°–96°	82 86	44 45 46
1,4-Diphenyl-1,3-butadiene	β-Nitrostyrene		in o-dichlorobenzene	m.p. 130°	40 80	44 46 48

TABLE 3. contd.

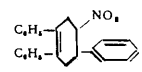
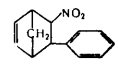
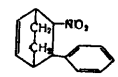
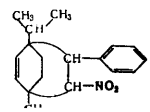
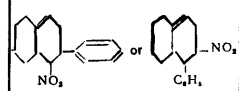
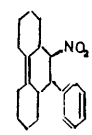
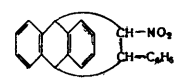
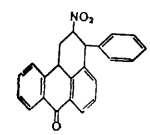
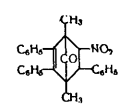
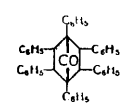
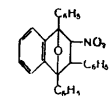
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield, %	Reference
2,3-Diphenyl-1,3--butadiene	β-Nitrostyrene		refluxing in *o*-dichlorobenzene	m.p. 175°	9	44 46
Cyclopentadiene	β-Nitrostyrene		without solvent	b.p. 145°/1 mm Hg	95 quant.	44 46
Hexachlorocyclo-pentadiene	β-Nitrostyrene	–	20–30 h, 100°–150°	–	0	11
Cyclohexadiene	β-Nitrostyrene		without solvent	b.p. 138°–142°/1 mm Hg	20 25	44 46
Phellandrene	β-Nitrostyrene		without solvent	m.p. 85°; b.p. 190°/1 mm Hg	45	44 46
Vinylcyclohexene	β-Nitrostyrene		–	–	–	48
Bicyclohexenyl	β-Nitrostyrene		8 h, 100°	m.p. 187°	96	49
Anthracene	β-Nitrostyrene		refluxing in xylene for 20 h	m.p. 150°–151°	54	41
Methyleneanthrone	β-Nitrostyrene		refluxing in acetic acid for 16 h	m.p. 255°	3	44 46
3,4-Diphenyl-2,5--dimethylcyclo-2,4--pentadien-1-one	β-Nitrostyrene		in benzene	m.p. 176°	92	9
2,3,4,5-Tetraphenyl-cyclo-2,4-pentadien--1-one	β-Nitrostyrene		refluxing in trichlorobenzene	–	–	44
Furan	β-Nitrostyrene	–	100°	–	0	46
2-Methylfuran	β-Nitrostyrene	–	100°	–	0	46
2,5-Dimethylfuran	β-Nitrostyrene	–	100°	–	0	46
1,3-Diphenylisobenzo-furan	β-Nitrostyrene		refluxing in ethanol for 3 h	m.p. 163°	quant.	46

TABLE 3. contd.

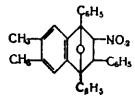
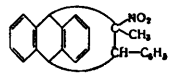
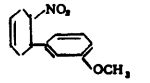
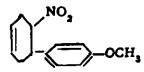
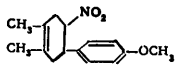
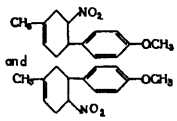
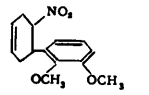
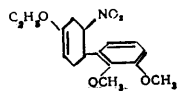
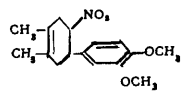
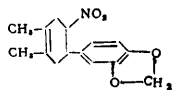
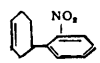
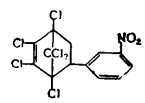
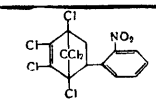
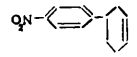
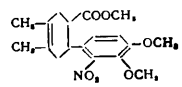
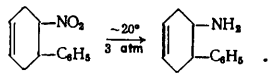
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield, %	Reference
1,3-Diphenyl-5,6-dimethylisobenzofuran	β-Nitrostyrene		refluxing in ethanol for 3 h	m.p. 182°	quant.	46
Anthracene	β-Methyl-β-nitrostyrene		refluxing in *o*-dichlorobenzene for 4 h	m.p. 171.5°–172°	1.4	41
1,3-Butadiene	*m*-Methoxy-β-nitrostyrene		4.5 days in toluene at 100°	m.p. 67°–90°	97	45
1,3-Butadiene	*p*-Methoxy-β-nitrostyrene		4 days in toluene at 100°	m.p. 76.5°–77.5°	82	45
2,3-Dimethyl-1,3-butadiene	*p*-Methoxy-β-nitrostyrene		in toluene at 100°	m.p. 103.5°–104°	92	4
Isoprene	*p*-Methoxy-β-nitrostyrene		in toluene at 100°	m.p. 74°–75° and 97.5°–98.5°	63	4
1,3-Butadiene	2,3-Dimethoxy-β-nitrostyrene		3 days at 120°–130°; in xylene for 14 h at 200°; 10 h in xylene; 175°–180°, in autoclave	m.p. 81°–82°; 81°–83° 91°	100 70	45 47 48
2-Ethoxy-1,3-butadiene	2,3-Dimethoxy-β-nitrostyrene		15 h in xylene at 200°	b.p. 195°–205°/0.1 mm Hg	81	47
2,3-Dimethyl-1,3-butadiene	3,4-Dimethoxy-β-nitrostyrene		10 h in xylene at 175°–180°, in autoclave	m.p. 129°–130°	80	48
2,3-Dimethyl-1,3-butadiene	3,4-Methylenedioxy-β-nitrostyrene		10 h in xylene, 175°–180°, in autoclave	m.p. 91°	70	48
1,3-Butadiene	*o*-Nitrostyrene		40 h in a sealed tube at 123°–127°	m.p. 24°–25°	48	50
Hexachlorocyclopentadiene	*m*-Nitrostyrene		–	–	–	10
1,3-Butadiene	*m*-Nitrostyrene		40 h at 123°–127° in a sealed tube	m.p. 47.4°–47.6°	44	50

TABLE 3. contd.

Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield, %	Reference
Hexachlorocyclo-pentadiene	*o*-Nitrostyrene			–	–	10
1,3-Butadiene	*p*-Nitrostyrene		40 h at 123°–127° in a sealed tube	m.p. 87.2°–87.7°	60	50
2,3-Dimethyl-1,3-butadiene	Methyl-3,4-dimethoxy-6-nitrocinnamate		heating in xylene in a sealed tube	m.p. 155°–156°	–	51

The pure unsaturated amine (LX) can be obtained at low pressure and room temperature:



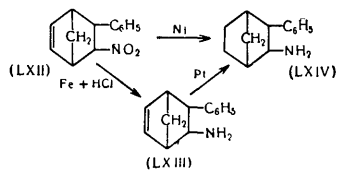
(LX)

The presence of two methyl group at the double bond considerably hinders its hydrogenation; for instance, in 1-nitro-2-phenyl-4,5-dimethylcyclohexene, the double bond is not hydrogenated below 165°.[52]

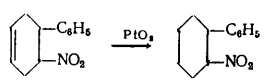
The degree of the selectivity of hydrogenation depends on the catalyst's "age" and the purity of the compound. Freshly prepared Raney nickel hydrogenates faster and more selectively than catalyst which has been standing for 2–3 months[52].

Methods are described in the literature for the selective reduction of either the nitro group[2] or the double bond[53] in nitro-adducts.

1-Nitro-2-phenylbicyclo[2,2,1]hexene (LXII) reduced with iron and hydrochloric acid gives in 47% yield the unsaturated amine (LXIII), which on hydrogenation over platinum yields the saturated amine (LXIV). LXIV can be obtained directly from (LXII) by hydrogenation over Raney nickel[2]:



If platinum oxide is used as a catalyst, selective hydrogenation of the double bond in 1-nitro-2-phenylcyclohexene (LXV) can be effected, while preserving the nitro group intact[53]:



(LXV)

On the basis of Arnold and Richardson's work[54], Zimmerman and Nevins[53] ascribed the *trans*-configuration to the adduct obtained from butadiene and β-nitrostyrene. This was in agreement with the fact that the hydrogenation of that adduct over platinum oxide in an ethyl acetate-acetic acid mixture, yielded *trans*-1-nitro-2-phenylcyclohexane.

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Δ^3-PIPERIDEINES

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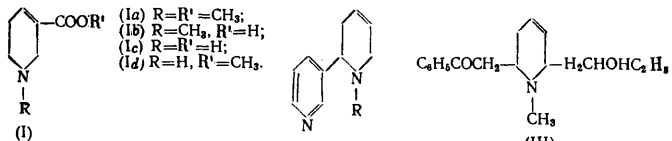
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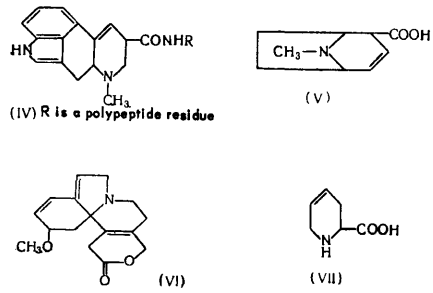
INTRODUCTION

Interest in the chemistry of 1,2,5,6-tetrahydropyridines (Δ^3-piperideines) is mainly due to the existence of a number of alkaloids which contain this structure. The fruit of the palm *Areca catechu*, which grows in India, Ceylon, and the Malay and Philippine Islands, is the source of a considerable number of alkaloids[1]. Jahns[2-5] obtained arecoline (*Ia*) and arecaidine (*Ib*) in a pure form from this fruit, and showed that they are both tetrahydropyridines methylated on the nitrogen and containing a carboxymethyl and a carboxy group respectively. Jahns believed that the double bond was in the 2,3-position, but Meyer[6,7] established that it is actually in the 3,4-position, and this has been confirmed synthetically by Wohl and Johnson[8]. Arecoline has been shown to be the methyl ester of 1-methyl--1,2,5,6-tetrahydronicotinic acid. Jahns also obtained guvacine and arecaine from the areca palm fruit; it was later shown[9-12] that guvacine is norarecaidine, i.e. 1,2,5,6--tetrahydronicotinic acid (*Ic*), and that arecaine is a mixture of arecaidine and guvacine. Hess[13] found another alkaloid related to arecoline, which has been named guvacoline (*Id*) and is norarecoline, i.e. 1,2,5,6-tetrahydronicotinic acid methyl ester.

The tobacco (*Nicotiana*) alkaloids anatabine (*IIa*)[14,15] and *N*-methyl anatabine (*IIb*)[16] are also Δ^3-piperideine derivatives; the secondary alkaloids from *Lobelia inflata* lobinine[17] and isolobinine[18-20] are stereoisomers of structure (III).[21]

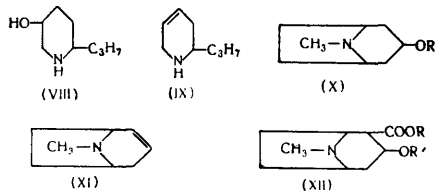


The Δ^3-piperideine nucleus is found in the ergot (*Secale cornutum*) alkaloids ergotoxine, ergotamine, ergometrine, etc. of general formula (IV)[22,23], and in anhydroecgonine (V), of which the ethyl ester has been found in waste materials from the production of minor alkaloids of the leaves of *Erythroxylon coca*[24] and the methyl ester separated from Peruvian and Javanese coca seeds[25]. The *Erythrina* alkaloid β-erythroidine, to which Boekelheide and coworkers[26,27] give the formula (VI), also contain the Δ^3-piperideine nucleus. The amino-acid baikiain[28] (L-1,2,3,6-tetrahydropyridine-2-carboxylic acid) (VII) has been separated from Rhodesian teak (*Baikiaea plurijuga*).



The structure of certain alkaloids contains a piperidine ring substituted in the 3- or 4-position by a hydroxyl group, which is often esterified; dehydrating agents convert these compounds into the corresponding Δ^3-piperideines. Thus pseudoconiceine (IX) is obtained by the action of phosphorus

pentoxide on pseudoconhydrine (VIII) from hemlock[29-31]. Dehydration of tropine (X*a*), obtained by the hydrolysis of atropine and hyoscyamine (X*b*)[32-34], produces tropidine (XI)[35-38], whose structure was largely elucidated by Willstätter[39].



(VIII) (IX) (X)

(XI) (XII)

(X*a*) R=H; (X*b*) R=COCHCH$_2$OH (C$_6$H$_5$); (XII*a*) R=R′=H;

(XII*b*) R=CH$_3$, R′=C$_6$H$_5$CO.

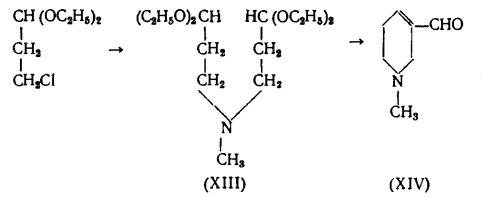
Anhydroecgonine (ecgonidine) (V) has been synthesised by the action of PCl_5 [40] or $POCl_3$ [41] on ecgonine (XII*a*) or directly from cocaine (XII*b*).[42] A number of studies[43-45] have been devoted to the structure of anhydroecgonine, but it has not yet been settled whether the carboxyl group is in the 3- or the 5-position of the piperideine nucleus. Decarboxylation of ecgonidine produces tropidine (XI)[46]; this transformation relates the alkaloids of the cocaine group to atropine.

Arecoline, the main areca palm alkaloid, has a physiological action similar to those of muscarine, acetylcholine, pilocarpine, and eserine, showing parasympathetic stimulation and acting on the majority of parasympathetically innervated organs. Arecoline reduces the blood pressure, increases salivation, and causes myosis of the eye[47]. It is used as a myotic preparation, but its main application is in veterinary practice as a purgative and anthelmintic[48]. Isolobinine exhibits a weak nicotine-like action; it stimulates breathing and raises the blood pressure (in large doses it paralyses the central nervous system and causes cessation of breathing)[49]. The ergot alkaloids are widely used in medicine, mainly in obstetrics and gynaecology[50,51]. β-Erythroidine has a considerable curare-like action[52]. Because of the great practical value of compounds containing the Δ^3-piperideine ring, many publications have dealt with the synthesis of systems of this type.

SYNTHESIS FROM HALOGENO- OR HYDROXY-PIPERIDINES

1,2,5,6-Tetrahydropyridines have generally been synthesised by preparing the corresponding 3- or 4-substituted piperidines followed by dehydration or dehydrohalogenation (certain syntheses of this type have already been mentioned). The elegant methods used for such syntheses have only achieved practical application in individual cases, but most of these syntheses have independent scientific interest.

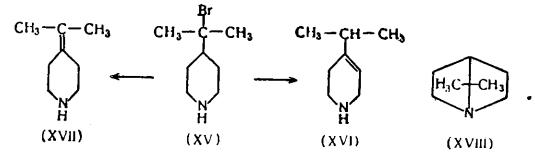
Arecaidine was first synthesised by Wohl and Johnson[8,53], who utilised the easy cyclisation of certain aminoacetals in an acid medium. The acetal of β-chloropropionaldehyde, prepared from acrolein, condenses with methylamine to form the diacetal of β-methyliminodipropionaldehyde (XIII), which is converted by the action of acid into 1-methyl-Δ^3-piperideine-3-aldehyde (XIV) and then to arecaidine by way of the oxime and nitrile. The same method has been used to prepare guvacine, 1-ethylguvacine, and a number of analogous compounds[54-61].



(XIII) (XIV)

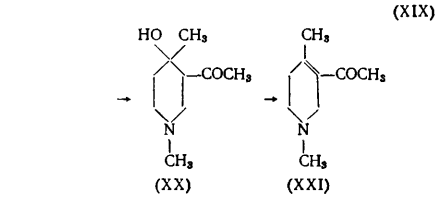
Hess and Leibbrandt[11] described a preparation of arecaidine by bromination of 1-methylnipecotinic acid methyl ester, removal of hydrogen bromide from the resulting 3-bromo derivative, and hydrolysis of the arecoline formed. However, Preobrazhenskii and Fisher[62] repeated this procedure and showed that the ester obtained after bromination and treatment with alkoxide is not arecoline, but the unchanged ester of 1-methylhexahydronicotinic acid.

The synthesis of a number of substituted Δ^3-piperideines by the removal of hydrogen halide with reagents, mainly basic, has been described[63-69]. Pauly and Harries[70] treated 2,4,6-trimethyl-4-iodopiperidine with silver mandelate to obtain the salt of the corresponding piperideine with mandelic acid. Removal of hydrogen bromide from 2-bromo-2-(4′-piperidyl)propane (XV) produced not the expected 7,7-dimethyl-1-azabicyclo[2,2,1]heptane (XVIII), but 4-isopropyl-Δ^3-piperideine (XVI) and 4-isopropylidenepiperidine (XVII).[71]



(XVII) (XV) (XVI) (XVIII)

By condensing acetone, formaldehyde, and methylamine hydrochloride, Mannich and Ball[72] obtained the aminoketone (XIX). Dilute hydrochloric acid induced this to undergo an aldol condensation to produce the compound (XX) (the conditions for this reaction — a comparatively low temperature and a weakly acid medium — are very reminiscent of biological conditions); the latter is easily dehydrated to 4-methylarecolone (XXI) (see also Mannich and Ritsert[73]). Other arecolones have been prepared similarly[74,75]. The barium hypobromite oxidation of (XX) gives the corresponding acid, which was converted to 4-methylarecoline by dehydration and methylation[76].

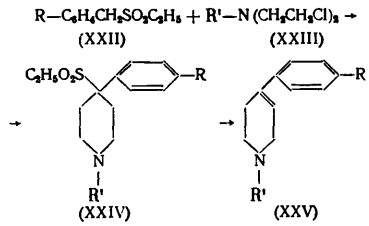


(XIX) (XX) (XXI)

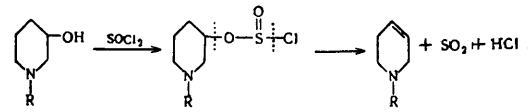
Starting from formaldehyde, acetaldehyde, and methylamine hydrochloride, and using the same method, has given arecaidine aldehyde in ~ 20% yield; in this case dehydration of the intermediate piperidine takes place spontaneously[77]. Similar methods for the synthesis of other Δ^3-piperideines have been described[78,79].

The condensation of sulphones containing an active methylene group (XXII) with β,β′-dichlorodiethylamines (XXIII)

gives compounds (XXIV), which on hydrolysis and dehydration afford alkyl derivatives of 4-phenyl-1,2,5,6-tetrahydropyridine (XXV).[80,81]



Paul and Tchelitcheff[82] found that thionyl chloride partially dehydrates 3-piperidols, leading to the formation of 1,2,5,6-tetrahydropyridines; in certain cases this reaction may be used preparatively. They suggest that a chlorosulphinic ester is formed as an intermediate rather than a chloropiperidine, since removal of hydrogen chloride from the latter takes place under completely different conditions.



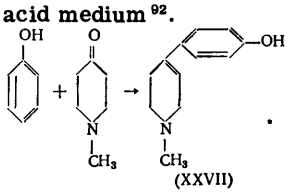
On analogous treatment, 1-ethyl-4-piperidol is converted directly to the chloro derivative, which gives up hydrogen chloride only by the action of sodium methoxide, forming the corresponding Δ^3-piperideine in low yield[68].

The organo-metallic synthesis with piperidones gives tertiary alcohols, which can be easily dehydrated to Δ^3-piperideines. Thus 1-methyl-4-(2'-thienyl)-Δ^3-piperideine (XXVI) has been prepared by the action of thienyl lithium on 1-methyl-4-piperidone and subsequent dehydration[83,84-91].



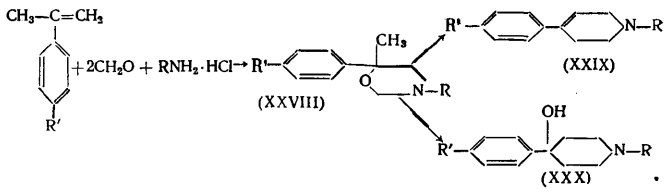
(XXVI)

1-Methyl-4-(4'-hydroxyphenyl)-Δ^3-piperideine (XXVII) has been prepared by the reaction of 1-methyl-4-piperidone with phenol in an acid medium[92].



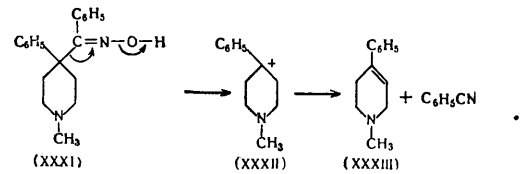
(XXVII)

Schmidle and Mansfield[93,94] have shown that 3-alkyl-6-methyl-6-aryltetrahydro-1,3-oxazines (XXVIII) (the condensation products of a substituted α-methylstyrene, formaldehyde, and a salt of a primary alkylamine) are converted by the action of acid to 1-alkyl-4-aryl-1,2,5,6-tetrahydropyridines (XXIX) in yields up to 82%.



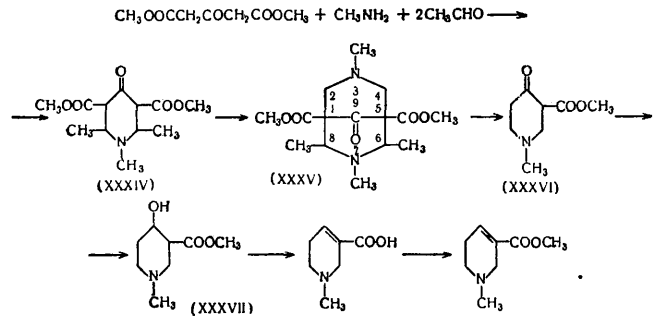
If an excess of acid is not used in this reaction, the corresponding piperidols (XXX) are formed; these may be dehydrated to the piperideines.

Under the conditions of the Beckmann rearrangement, 1-methyl-4-phenyl-4-piperidyl phenyl ketoxime (XXXI) decomposes to form benzonitrile and 1-methyl-4-phenyl-Δ^3-piperideine (XXXIII); this reaction apparently proceeds by way of the carbonium ion (XXXII), which becomes stabilised by the loss of a proton[95].



A number of other syntheses of Δ^3-piperideines by dehydration of the piperidols have been described[96-101].

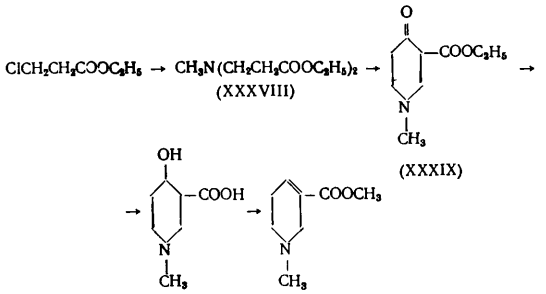
The preparation of arecaidine by the dehydration of 1-methyl-4-hydroxypiperidine-3-carboxylic acid has been reported[102]. Ugryumov has developed a method for the synthesis of this acid[103], and has used it to prepare arecaidine and arecoline. In this method, dimethyl acetone dicarboxylate is condensed with acetaldehyde and methylamine to give dimethyl 1,2,6-trimethyl-4-piperidone-3,5-dicarboxylate (XXXIV), which reacts with methylamine and formaldehyde to form dimethyl 3,6,7,8-tetramethyl-9-oxobispidine-1,5-dicarboxylate (XXXV). On heating with hydrochloric acid, methyl 1-methyl-4-piperidone-3-carboxylate (XXXVI) is formed, which, on catalytic reduction, gives methyl 1-methyl-4-hydroxypiperidine-3-carboxylate (XXXVII). Arecaidine is then obtained by the action of acid, and esterification produces arecoline.



Recently Maurit and Preobrazhenskii[104] studied various methods of reduction of the keto-ester (XXXVI) and the configurations of the resulting piperidols.

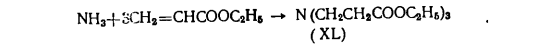
Dankova, Sidorova, and Preobrazhenskii[105] devised a preparative synthesis of arecoline, based on McElvain's method[105]. Ethyl β-chloropropionate reacts with methylamine to form β,β'-diethoxycarbonyldiethylmethylamine (XXXVIII), which is cyclised by sodium isoamylate. The resulting 1-methyl-3-ethoxycarbonyl-4-piperidone (XXXIX) is reduced with Raney nickel or with sodium amalgam in an

acid medium; subsequent dehydration and esterification give arecoline.

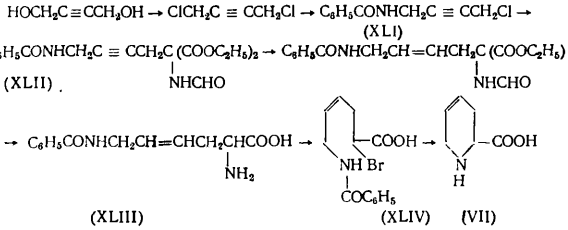


Dobrowsky[107] published an analogous synthesis of arecoline, compound (XXXVIII) being obtained by the condensation of ethyl acrylate with methylamine; the procedure was altered slightly and slightly higher yields were obtained. The method (starting from methyl acrylate) has recently been further improved and applied to the synthesis of a number of homologues of arecoline[108]. Acrylonitrile may be used in place of the acrylic esters in this and similar syntheses[109,110].

A similar method has been described for the preparation of guvacine[111]. Three molecules of ethyl acrylate are reacted with one of ammonia, the resulting β, β', β''-triethoxycarbonyltriethylamine (XL) is cyclised to piperidone, and the latter is reduced, hydrolysed, dehydrated, and esterified in a process similar to that described above. This method had already been used by Ugryumov to prepare 2,6-dimethylarecoline[112].



In 1958 racemic baikiain (VII) was synthesised[113]. The starting material was 1,4-dichloro-2-butyne, which was converted by the action of urotropine and then benzoyl chloride into 1-benzamido-4-chloro-2-butyne (XLI). This reacted with the sodium derivative of formylaminomalonic ester to give compound (XLII). Further steps in the reaction sequence comprised the partial hydrogenation of (XLII), hydrolysis, and decarboxylation, and produced the amino-acid (XLIII) of the *cis*-configuration. Replacing the amino group by bromine by the action of nitrosyl bromide gave *cis*-1-bromo-5-benzamido-3-pentene-1-carboxylic acid (XLIV), which was cyclised by $Ba(OH)_2$ to *dl*-baikiain (VII).



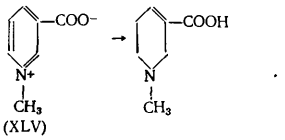
The main disadvantages of these syntheses are, as already mentioned above, their complexity and the large number of steps involved, which cause low yields of the final products.

SYNTHESIS BY THE REDUCTION OF PYRIDINE DERIVATIVES

The preparation of Δ^3-piperideine derivatives by the partial reduction of the corresponding pyridine derivatives is of considerable interest. It is known that reduction of the pyridine ring produces not only the completely hydrogenated derivatives, but also partially reduced compounds, including Δ^3-piperideines. Many methods exist for the hydrogenation of the pyridine nucleus, but only a few are of preparative value.

Catalytic Reduction

It is practically impossible with this reduction method to stop the reaction at the required stage; hydrogenation proceeds to the hexahydropyridine stage, the yields of 1,2,5,6-tetrahydropyridines being insignificant. Thus the yield of arecaidine by the reduction of trigonelline (XLV) over platinum black[114] does not exceed 1%.



Mumm[115-117] obtained similar results for pyridines but showed that substituted pyridinium salts are reduced in the presence of platinum to Δ^2-piperideines, which on distillation in vacuum isomerise to Δ^3-piperideines. Catalytic hydrogenation of 1,2-dihydropyridines over platinum black gives tetrahydro-derivatives in which the double bond is probably in the 3,4-position[118,119]. The hydrogenation of methyl isonicotinate methiodide over platinum oxide is said to produce methyl 1,2,5,6-tetrahydroisonicotinate[120].

Electrolytic Reduction

This method of reduction gives somewhat better results. Davies and McGee[121] separated 10% of Δ^3-piperideine and a small quantity of tetrahydropicoline from commercial piperidine; they suggest that these compounds are formed in the electrolytic reduction of pyridine containing homologues as impurities. The electrolytic reduction of pyridine and its quaternary salts in an acid medium has given ~ 20% of tetrahydro derivatives[122,123]. Šorm[124] and Ferles[125] reduced α-, β-, and γ-picolines, 2,6-lutidine, and picolinic, nicotinic, and isonicotinic acids electrolytically, obtaining the 1,2,5,6-tetrahydro-derivatives in yields of 10–58%; trigonelline was reduced to arecaidine in satisfactory yield. In the course of this reaction, decarboxylation products appear and hexahydro-derivatives are also formed[126].

Reduction by Sodium and Alcohols

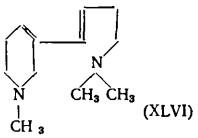
In 1902 Chichibabin reported[127] that the reduction of 4-benzylpyridine with sodium in alcohol produced a small amount of the tetrahydropyridine as well as the corresponding piperidine. The same phenomenon occurs, but to a lesser extent, in the reduction of 2-benzylpyridine. Similar results were later reported for the reduction of 4-methyl-3-ethylpyridine and certain other compounds[128-130]. In 1950 Lukeš and Ernest[131], attempting to prepare *s*-butylpiperidine by reducing the corresponding pyridine with sodium in amyl alcohol, obtained a mixture of the hexa- and tetrahydro-compounds. Wawžonek and coworkers[132] generalised the earlier results and developed the reduction of pyridines with sodium in butyl alcohol as a preparative method for Δ^3-piperideines (see also Lukeš and Ferles[133]). The yields

are high (57–87%), but only when the pyridine contains a 4-alkyl substituent, which considerably limits the applicability of the method.

Reduction by Mixed Metal Hydrides

Panouse[134-137] studied the reduction of alkyl pyridine halides with potassium borohydride, and found that pyridine methiodide is converted to 1-methyl-Δ^3-piperideine in 65% yield. Increasing the chain length of the *N*-alkyl radical favours side reactions, leading to the formation of various boron complexes, dihydropyridine dimers, etc.; however, the yields of Δ^3-piperideines are usually satisfactory (40–74%). Ferles[138] obtained similar results with sodium borohydride. Lyle and coworkers[139] described the preparation of 1-methyl-4-benzyloxy-Δ^3-piperideine from the corresponding quaternary salt in a yield of 86%. Panouse also reduced the methiodides of nicotinic acid, methyl nicotinate, and nicotinamide to arecaidine, arecoline, and arecaidine amide respectively, with yields of the order of 30% (see also Ferles[126]).

Nicotine methiodide is easily reduced to the tetrahydro-derivative; in this case there is a side reaction involving the opening of the pyrrolidine ring with the formation of the compound (XLVI). It should be noted that the reduction of pyridinium salts with potassium borohydride produces 1,2-dihydro-derivatives in a number of cases, particularly if the radical attached to the nitrogen is glycosidic in nature[137].

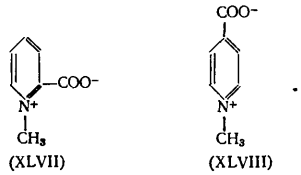

(XLVI)

Pyridinium salts can also be reduced to Δ^3-piperideines with lithium aluminium hydride. Panouse[137] showed that considerable amounts of the 1,2-dihydro-derivatives are usually formed, but this can be avoided by carrying out the reaction in tetrahydrofuran. The yields of Δ^3-piperideines are always lower than when using potassium borohydride. However, Ferles[126] succeeded in obtaining high yields of Δ^3-piperideines (up to 56%) by carrying out the reaction under conditions normal for lithium aluminium hydride reductions.

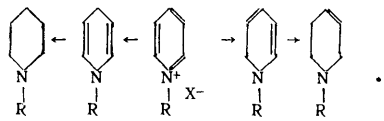
Reduction by Formic Acid

In 1936 Mayo[140] obtained a mixture of 1,1-dimethylpiperidinium formate and partially hydrogenated pyridines by the reaction of pyridine with formic acid and methyl alcohol under forcing conditions. Lukeš[141] showed that pyridine itself is not reduced by formic acid, but that reaction of pyridine methobromide with formic acid in the presence of potassium formate gives a mixture of 1-methylpiperidine and 1-methyl-Δ^3-piperideine, the first being predominant. It is assumed that in Mayo's work[140] it is not pyridine itself which is reduced, but the 1-methylpyridinium ion. It is interesting that, unlike pyridine, quinoline is reduced by formic acid (advantageously in the presence of sodium formate[142] or triethylamine[143]), forming 1-formyl-1,2,3,4-tetrahydroquinoline in good yield. Lukeš and coworkers have applied their method for the reduction of pyridinium salts[141,144] to the preparation of a number of alkyl- and aryl-substituted Δ^3-piperideines[145-149]. Kost, Yudin, and Shipov[150] applied this method to other alkylpyridinium halides.

Interesting attempts were made to reduce the pyridine carboxylic acids by this method, so as to obtain arecaidine and its isomers directly. However, in reducing homarin (XLVII) and trigonelline (XLV) (the methyl-betaines of picolinic and nicotinic acids) under forcing conditions, Lukeš[151] obtained only a mixture of decarboxylation products, i.e. 1-methyl-Δ^3-piperideine and 1-methylpiperidine. The reduction of the methyl-betaine of isonicotinic acid (XLVIII) gave 1-methylisonipecotinic acid, i.e. the pyridine ring had been completely hydrogenated. Reduction of *N*-carboxyalkylpyridinium halides gave only decarboxylation products[152].


(XLVII) (XLVIII)

Yields of the mixture of reduced pyridines obtained by Lukeš' method are usually high (~80%), but the Δ^3-piperideine content does not exceed 10% in the majority of cases; a very high yield (82%) of the Δ^3-piperideine was obtained only in the reduction of 1,4-dimethylpyridinium bromide[147]. According to Lukeš, the reduction of the pyridinium salts proceeds in two ways:



As a rule, hydrogen first adds on predominantly in the 1,4-position, and since the 2,3-double bond is easily reduced by formic acid, considerably more of the hexahydro-derivative is formed in these experiments than of the tetrahydro-derivative. Kost and coworkers[153] have shown that when potassium formate is replaced by triethylamine in the reduction of pyridinium salts by formic acid, more hydrogen adds initially in the 1,2-position. This enables alkyl-substituted Δ^3-piperideines to be obtained in yields of ~35%.

Other Methods of Reduction

Jahns[5] reduced trigonelline (XLV) with tin and hydrochloric acid, but the separation of arecaidine from the reaction mixture was complex and yields were low. Meyer[6] used sodium amalgam to prepare arecaidine, but it was later shown[114] that the yield by this method does not exceed 1%.

PROPERTIES OF Δ^3-PIPERIDEINES

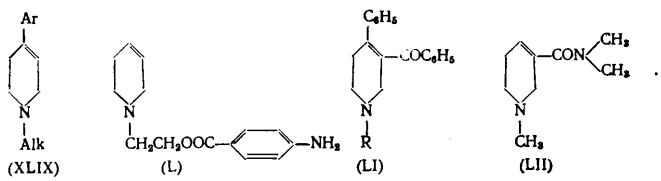
Δ^3-Piperideines possess all the normal properties of aliphatic amines and ethylenic compounds. They are fairly strong bases which easily form salts with various acids, can be acylated, alkylated, and nitrosated on the nitrogen, and form *N*-oxides (for the preparation of arecoline *N*-oxide see Shchukina and coworkers[154]). 1-Methyl-Δ^3-piperideine can be demethylated without rupture of the ring by the reaction with cyanogen bromide and hydrolysis of the resulting *N*-cyanide[155]. The Hofmann degradation of the quaternary ammonium bases formed by Δ^3-piperideines gives the

corresponding des-bases, and has been used for proving the structure of the original compounds[145,146,156]. Although the double bond of the Δ^3-piperideines is markedly more stable to reduction than the Δ^2 double bond, they are nevertheless easily hydrogenated in the presence of metal catalysts[11,65,66,75,86,124,132,157]; the content of Δ^3-piperideines in mixtures with piperidines can be determined by this method.

Δ^3-Piperideines easily add bromine to the double bond. The resulting dibromopiperidines are commonly used for separating piperideines from the corresponding piperidines; treatment of the dibromides with zinc quantitatively regenerates the Δ^3-piperideines[144-148,150,153]. The double bond of Δ^3-piperideines also adds malonic acid (usually in the 4-position)[59,61]; this method was used to synthesise cincholoiponic acid (3-carboxy-4-piperidylacetic acid)[58], obtained by the degradation of quinine. Treatment of arecoline with ammonia under pressure gives the amide of 1-methyl-4-aminopiperidine-3-carboxylic acid[158]. The hydration of Δ^3-piperideines to 4-piperidols[94] and the addition of hydrogen halides across the double bond to form 4-halopiperidines[96,129] have been described; the latter reaction was used to effect a series of conversions in a number of tropane alkaloids[38,159]. By the oxidation of guvacine under mild conditions with permanganate, Freudenberg[10] obtained a compound presumed to be 3,4-dihydroxypiperidine-3-carboxylic acid.

The double bond of Δ^3-piperideines is easily ozonolysed[145]; this reaction also can be used for the proof of structure. For this purpose, rather than the piperideines themselves, the corresponding des-bases (the Hofmann degradation products) are usually ozonolysed[146,156]. Δ^3-Piperideines can be dehydrogenated in the presence of zinc[5], selenium[78,160], or palladium[78] to the corresponding pyridines.

Certain synthetic analogues of arecoline and other natural Δ^3-piperideines are physiologically active. Thus 1-alkyl-4-aryl-Δ^3-piperideines (XLIX) possess analgesic activity, and some are as effective as codeine[91,161]. The Δ^3-piperideine derivative (L) and its analogues have been used as local anaesthetics[162]; compound (L) also has a nicotine-like action. Compounds of the type (LI) were found to be quite effective spasmolytics[88]. Studies of a number of close analogues of natural Δ^3-piperideines have led to certain conclusions about the way in which physiological activity depends on structure; one of the compounds studied was 1-methyl-1,2,5,6-tetrahydronicotinic acid dimethylamide (LII)[163].



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INVESTIGATION OF COMPLEX FORMATION IN SOLUTION BY THE DISTRIBUTION METHOD

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Extraction with non-aqueous solvents is very widely employed in solving various problems in chemistry and chemical technology. The separation of elements with closely similar properties, the concentration and isolation of micro- and ultramicro-concentrations of metals, the clear separation and identification of difficultly separable organic substances, show why many investigators have evinced interest, especially in recent years, in the study of extraction processes[1-5]. The solubility of internal complexes and of a number of complexes of metals with inorganic ligands in organic solvents makes it possible to utilise the distribution method as a reliable means of studying the composition and many other physicochemical characteristics of complex compounds.

The principles of the distribution (or extraction) method were laid down by Nernst (1891). In the first paper on the constancy of the partition coefficient for species of the same molecular composition distributed between two immiscible solvents, Nernst established[6] the possibility of using his distribution law to study the dissociation equilibria of a number of substances in aqueous solution. Shortly afterwards Hendrixson[7] studied the distribution of benzoic and salicylic acids between water and benzene or chloroform and determined the dissociation constants K_{diss} of these acids in the aqueous phase, their dimerisation constants K_{dim} in the organic phase, and their distribution constants (partition coefficients) K_{part} between organic and aqueous phases*:

$$[H^+][A^-] = K_{diss}[HA]_{aq} , \quad (1)$$

$$[HA]_{org} = K_{part}[HA]_{aq} , \quad (2)$$

$$[H_2A_2]_{org} = K_{dim}[HA]^2_{org} . \quad (3)$$

* HA = molecule of acid, A^- = anion of acid, and H_2A_2 = = dimer molecule. We shall use the symbolic formula HA to denote reagents which dissociate as monobasic acids.

At about the same time similar investigations were carried out with inorganic compounds, e.g. thiocyanates of iron and halides of mercury[8]. In this work, however, the authors do not consider the possible formation of charged complex species. As far as we know, the first attempt to explain the experimental results by a stepwise mechanism of complex formation was published by Morse in 1902.[9] After studying the distribution of mercury complexes between toluene and an aqueous phase containing halide ions (A^-), Morse came to the conclusion that the aqueous phase contains, apart from Hg^{2+} and uncharged HgA_2 molecules, positively charged HgA^+. Assuming the impossibility of extracting charged particles with an organic solvent, Morse calculated from his results the distribution constant λ_N for HgA_2 between the phases and the successive formation constants k_1 and k_2:

$$[MA_{n-1}^{N-n+1}][A^-]k_n = [MA_n^{N-n}] , \quad (4)$$

$$[MA_N]_{org} = \lambda_N[MA_N]_{aq} . , \quad (5)$$

where $M^{N+} = Hg^{2+}$ and A^- is the halide ion.

Although the possibility of using the distribution method to study complex compounds in solution has been demonstrated so long ago, no attempt was made before 1941 to formulate quantitatively the relation between the partition coefficients for a metal in a given system and the parameters of the latter (concentration of metal ions, pH of aqueous phase, concentration of reagent, etc.). In 1941 Kolthoff and Sandell[10], studying the dithizone derivatives of certain metals, attempted to establish such a relationship on the basis of the distribution law and the law of mass action. Assuming that only free (hydrated) metal ions M^{2+} are present in the aqueous phase and excluding the possibility of association of the molecules of dithizone and the complex MA_2 in either phase, these authors accepted the following equations as correct:

$$K'_{part\ HA} = \frac{[HA]_{aq}}{[HA]_{org}} , \quad (6)$$

$$K'_{part\ MA_2} = \frac{[MA_2]_{aq}}{[MA_2]_{org}} \quad (7)$$

(according to the conventions which are now generally adopted these quantities are the reciprocals of the distribution constants of HA and the complex MA_2).

$$M^{2+} + 2HA \rightleftarrows MA_2 + 2H^+ , \quad (8)$$

(in the aqueous phase)

$$\frac{[MA_2]_{aq}}{[M^{2+}]_{aq}}\frac{[H^+]^2_{aq}}{[HA]^2_{aq}} = K_{eq} . \quad (9)$$

Substituting the concentrations of MA_2 and HA in the aqueous phase from Eqns. (6) and (7), they established the expression

$$\frac{[MA_2]_{org}}{[M^{2+}]_{aq}}\frac{[H^+]^2_{aq}}{[HA]^2_{org}} = K_{eq}\frac{K'^2_{part\ HA}}{K'_{part\ MA_2}} = K, \quad (10)$$

by means of which they arrived at Eqn. (12) linking the partition coefficient of the metal q with the characteristics of the system:

$$q = \frac{[MA_N]_{org}}{\sum_{n=0}^{n=N}[MA_n]_{aq}} , \quad (11)$$

$$q = \frac{[MA_2]_{org}}{[M^{2+}]_{aq}} = K\frac{[HA]^2_{org}}{[H^+]^2_{aq}} . \quad (12)$$

As can be seen from Eqn. (12), the partition coefficient of a bivalent metal increases proportionally to the square of the concentration of the reagent in the organic phase and

decreases proportionally to the square of the hydrogen-ion concentration in the aqueous phase. Kolthoff and Sandell allowed for the effect of hydrolysis on the extraction process, and introduced into Eqn. (12) the appropriate correction term (for the case of a bivalent metal ion):

$$q = \frac{[MA_2]_{org}}{[M]_{aq\ total}} = K \cdot \frac{[HA]^2_{org}}{([H^+]^2_{aq} + \beta_1[H^+]_{aq} + \beta_2)}, \qquad (13)$$

where β_1 and β_2 are hydrolysis constants.

Eqn. (12), obtained by Kolthoff and Sandell, has been repeatedly criticised[11,12]. In fact, the authors not only leave out of consideration the successive formation of complex species, but also in general neglect any complexes of the metal in the aqueous phase, which restricts their arguments to a limited number of systems and a limited range of concentrations. In spite of these limitations, a number of authors have subsequently used Kolthoff's equation (without any special changes) in the study of the stability of the dithizone complexes of metals[13-17]. For example, Babko and Pilipenko continued Kolthoff's investigations by studying the physicochemical characteristics of dithizone and its complexes with zinc, cadmium, and lead[13,14]. Babko and his coworkers determined the composition of the dithizone complexes by measuring the optical density of the extract after appropriate dilution with the organic solvent used. The limitations of such a method of determining the composition of a complex compound distributed between two phases have been pointed out in the Russian literature[18].

Eve and Strasheim[19] studied the effect of the hydrogen-ion concentration on the extraction of the dithizone derivatives of zinc, cobalt, nickel, and copper from tartrate solutions by means of chloroform*. Substitution of their experimental values for the partition coefficient and other quantities in the Kolthoff equation showed that the extraction process in general obeys Eqn. (10).

Subsequently, Irving and Williams[11] and other investigators[22] somewhat extended our ideas on the mechanism of complex formation and, besides allowing for the distribution of the reagent between the two solvents and its dissociation in the aqueous phase, took into account the formation of an uncharged complex in aqueous solution:

$$\begin{array}{ccc} H^+ + A^- \rightleftarrows & & HA \\ M^{N+} + NA^- \rightleftarrows MA_N & & \Big\uparrow\Big\downarrow \\ \Big\downarrow\Big\uparrow & & HA \\ MA_N & & \end{array} \quad \begin{array}{l} \text{in aqueous phase} \\ \text{in organic phase} \end{array} .$$

Irving put forward a simple quantitative treatment of the experimental results which took into account the relationship between the partition coefficient of the metal and the concentration of the reagent, the dissociation constant of the latter, the pH of the aqueous phase, the partition coefficient of the complexes, and other parameters of the system. If HA behaves as a monobasic acid over a given pH range and if the only complexes in the aqueous and organic phases are the mononuclear complexes MA_N, the relationship between q and the parameters of the system is represented by the simple equation

$$q = \frac{[MA_N]_{org}}{[MA_N]_{aq} + [M^{N+}]_{aq}} = \frac{1}{K'_{part\ MA_N} + ([H^+]^N_{aq}\ K \cdot [HA]^N_{org})}, \qquad (14)$$

where

$$K = \frac{(K_{diss\ HA}\ K'_{part\ HA})^N}{K_{inst.\ MA_N}\ K'_{part\ MA_N}}, \qquad (14a)$$

and $K_{inst\ MA_N}$ — the overall instability constant of the complex MA_N — is defined by the equation

$$K_{inst.\ MA_N} = \frac{[M^{N+}][A^-]^N}{[MA_N]}. \qquad (15)$$

It can be easily shown that, if

$$K'_{part\ MA_N} \ll \frac{[H^+]^N_{aq}}{K \cdot [HA]^N_{org}},$$

Eqn. (14) passes into the above Eqn. (12) of Kolthoff. Irving and Williams calculated the magnitude of the error due to neglecting the existence of MA_N complexes in the aqueous phase, and examined in detail the effect of change in pH, reagent concentration, and other factors on the extraction of various metals.

On the basis of the relationships deduced, Irving and his coworkers investigated complex formation between zinc and dithizone[23,24] and discussed earlier results[25]. The composition of the dithizone derivative of zinc was established from the graph of $\log q$ against $\log([HA]_{org} + pH)$ and spectrophotometrically by the method of continuous variations[26]. Buffered mixtures of varying composition were used in the work, which might have led to secondary complex formation and diminished the reliability of the results. No attempt was made in the above work, however, to examine in a general way the various processes of complex formation and distribution occurring in two-phase systems.

During the last ten years, the Scandinavian chemists, the Irving school and a number of other investigators (Diamond, Connick, etc.), whose work will be examined below, have extended the theoretical equipment required to calculate the characteristics of various types of complex from distribution data.

In its modern form, the distribution method consists of the study of the partition coefficients of a metal between immiscible solvents as a function of one or several variables. The process of extraction of a metal from an aqueous phase by means of an organic solvent is affected by many factors, such as the concentrations of ions of the element investigated and of other cations in the solution, of various anions, and of hydrogen ions, the nature of the organic solvent, etc. In most cases the partition coefficient depends in a complicated way on these variables.

In the treatments referred to above, one of the variables was generally examined, and a more or less satisfactory explanation given for the results obtained. The general picture was that the metal ion M^{N+} reacts in aqueous solution with the ligand A^- and the resulting complex MA_N is distributed between the phases. In fact complexes with different compositions and different charges exist in aqueous solution, and the complex (or series of complexes) extracted may include in their composition solvent molecules and other components. Preparative methods give no accurate indication either of the composition of the complexes in solution or even of the existence of many complexes, which in general exist only in solution. Analysis

* Many investigators have published papers on the role of pH in the extraction of internal complexes. Korenman and Sheyanova[20,21] attempted to obtain a theoretical basis for the influence of pH on the yield of reaction product in complex formation between metal ions and organic reagents.

of solid preparations sometimes shows the existence of extremely complicated compounds, containing metallic, A^-, and OH^- ions, uncharged molecules of HA, H_2O, organic solvent, etc. For example, the compounds $Th(OH)_2CrO_4 \cdot H_2O$,[27] $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$,[28] etc. are known. The isolation of a compound in the solid form, however, does not always prove its existence in solution. In the second of these substances the benzene molecules are only held in the spaces between the $Ni(CN)_2 \cdot NH_3$ molecules, and are linked to the latter by weak van der Waals forces. In solution, however, $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$ molecules do not exist at all or else their number is insignificant. A similar position is observed with hydroxyquinoline molecules in the compound $ScA_3 \cdot HA$,[29] where A represents the quinolinoxy ion. Definite conclusions as to the composition of the complexes which are extracted and those which are in the aqueous phase can be drawn only on the basis of a physicochemical analysis of the solutions. Practically all the fundamental characteristics of complexes can be obtained by studying the distribution of the metal when the variables enumerated above are changed. Until recently the opinion was expressed that the distribution method could be used only to ascertain the comparative stability of complex compounds, and doubt was entertained as to its suitability for the quantitative determination of their stability constants[30].

In 1949 Rydberg and other Scandinavian investigators demonstrated the full value of the distribution method for the quantitative study of complex formation in solution. To interpret data relating to the extraction of a metal complex by an organic solvent from an aqueous phase of low and constant ionic strength, these authors took into account the influence of temperature and examined the following variables: concentrations of metal ion M^{N+}, anion A^-, HA, OH^-, and solvents [organic (Org) and H_2O].[31-33] In the general case complexes of type I may be formed in aqueous solution (the charges on the ions are omitted):

$$\underset{(I)}{M_mA_n(OH)_p(HA)_r(Org)_s(H_2O)_t},$$

and their formation constants may be written in the general form

$$\kappa_{m,n,p,r,s,t} = \frac{[M_mA_n(OH)_p(HA)_r(Org)_s(H_2O)_t]}{[M]^m[A]^n[OH]^p[HA]^r[Org]^s[H_2O]^t} \quad . \qquad (16)$$

Taking into account the interrelationship of some of the variables in Eqn. (1), and the ionic product of water,

$$[H_2O]\ K_{H_2O} = [H^+][OH^-] \quad , \qquad (17)$$

Eqn. (16) can be written in the form

$$\kappa_{m,n,p,r,s,t} = \frac{[M_mA_n(OH)_p(HA)_r(Org)_s(H_2O)_t]}{[M]^m[HA]^{n+r}[H]^{-n-p}[H_2O]^{p+t}[Org]^sK^n_{\text{diss HA}}K^p_{H_2O}} \quad . \qquad (18)$$

Writing $n + r = x$, $n + p = y$, and $p + t = z$, formula I can be rewritten in a simpler form:

$$\underset{(II)}{M_m(HA)_x(H)_{-y}(H_2O)_z(Org)_s} \quad .$$

In the majority of cases it is quite difficult to determine the number of water molecules incorporated in a complex in aqueous solution. However, it can be found by an indirect method if we know the coordination number of the element with respect to all the ligands in the complex, and also the number of coordination positions occupied by all the ligands other than H_2O. Usually all experiments are carried out at constant ionic strength, and the effect of hydration is normally included in the formation constant for the complex. In such a case complex II can be written in a still simpler form:

$$\underset{(III)}{M_m(HA)_x(H)_{-y}(Org)_s},$$

and the formation constant of the complex is represented by the equation

$$\kappa_{m,x,y,s} = \frac{[M_m(HA)_x(H)_{-y}(Org)_s]}{[M]^m[HA]^x[H]^{-y}[Org]^s} \quad . \qquad (19)$$

The physical meaning of x and y is clear: x is equal to the total number of HA and A^-, and y the total number of A^- and OH^- per atom of complex-forming metal. The charge on the complex is then $mN - y$. All the subsequent arguments of Rydberg are based on the assumption that only uncharged complexes pass into the organic solvent. This assumption is correct for solvents of low dielectric constant. When it is known that only a neutral complex will pass into the organic layer (distribution constant $\lambda_{m,x,-mN,s}$), and the mole fraction of the solvents is constant (ionic strength I = = const.), the partition coefficient for the metal can be written in the form

$$q = \frac{\sum_1^m \sum_0^x \sum_0^s m\kappa_{m,x,mN,s}\ \lambda_{m,x,mN,s}\ [M]^m[HA]^x[H]^{-mN}[Org]^s}{\sum_1^m \sum_0^x \sum_0^y \sum_0^s m\kappa_{m,x,y,s}\ [M]^m[HA]^x[H]^{-y}[Org]^s} \quad . \qquad (20)$$

Eqn. (20) is greatly simplified if only mononuclear complexes are considered. For the majority of metallic ions, other than those which are strongly hydrolysed, it is legitimate to ignore polynuclear complexes ($m > 1$), provided that the experiments are carried out with $[M] \leqslant 10^{-3}$ g-ion/litre. A range of concentrations of metal ions can usually be found in which formation of polynuclear complexes, hydrolysis products, or polymeric forms can be neglected. The search for such a range reduces to a study of the dependence of the partition coefficient on the concentration of metal ions in the aqueous phase with other conditions the same. If it is established that q does not depend on the metal-ion concentration over a given range, the formation of polynuclear complexes can be safely ignored. In the work of Rydberg only mononuclear complexes are considered. In both the Russian and foreign literature methods have already been described for studying the composition and characteristics of several systems containing polynuclear complexes[34-39]. Such a study can be carried out by means of distribution, spectrophotometric, etc. methods. The equations considered below are applicable only if it has been established that q is independent of the metal-ion concentration.

The distribution method enables us to elucidate the influence of the organic solvent on the distribution of the metal, and also to establish whether the water-immiscible solvent molecules enter the complex. The effect of the organic solvent can be ascertained by varying $[Org_1]$ by adding a third component Org_2, also immiscible with water. However, even if this third component does not interact with the complex, its addition may cause a considerable change in the activity coefficients. A different approach is possible, consisting in a study of the distribution of the metal in the two systems H_2O-Org_1 and H_2O-Org_2 for identical hydrogen-ion and reagent concentrations. If mononuclear complexes are formed in both systems, the ratio of

the partition coefficients for the metal is given by the following expression:

$$\frac{q_1}{q_2} = \frac{\sum_0^x \sum_0^s \kappa_{x,N,s}\ \lambda'_{x,N,s}\ [HA]^x [H]^{-N} [Org_1]^s \sum_0^x \sum_0^y \sum_0^s \kappa''_{x,y,s}\ [HA]^x [H]^{-y} [Org_2]^s}{\sum_0^x \sum_0^s \kappa''_{x,N,s}\ \lambda''_{x,N,s}\ [HA]^x [H]^{-N}\ \ Org_2]^s \sum_0^x \sum_0^y \sum_0^s \kappa'_{x,y,s}\ [HA]^x [H]^{-y} [Org_1]^s}, \quad (21)$$

where κ' and κ'' are the formation constants and λ' and λ'' the distribution constants for the complexes in the two systems. At constant ionic strength under equilibrium conditions $[Org_1]$ = const. and $[Org_2]$ = const., and we may therefore write

$$\kappa'_{x,y} = \sum_0^s \kappa'_{x,y,s}\ [Org_1]^s, \quad (22)$$

and analogous expressions for $\kappa''_{x,y}$, $\kappa'_{x,N}\lambda'_{x,N}$, and $\kappa''_{x,N}\lambda''_{x,N}$. After substitution of these in (21), the latter simplifies to

$$\frac{q_1}{q_2} = \frac{\sum_0^x \kappa'_{x,N}\ \lambda'_{x,N}\ [HA]^x [H]^{-N} \sum_0^x \sum_0^y \kappa''_{x,y}\ [HA]^x [H]^{-y}}{\sum_0^x \kappa''_{x,N}\ \lambda''_{x,N}\ [HA]^x [H]^{-N} \sum_0^x \sum_0^y \kappa'_{x,y} [HA]^x [H]^{-y}}. \quad (23)$$

If complexes are formed with one or both solvents $\lambda'_{x,N} \neq \lambda''_{x,N}$ and with rare exceptions $\kappa'_{x,N} \neq \kappa''_{x,N}$, and the ratio q_1/q_2 will change with change in [H] when [HA] = const. and vice versa.

If under these conditions q_1/q_2 = const., it can be regarded as established that the complex contains no solvent molecules*. Fig. 1 shows the curves for $\log q = f(pH)$: in the case of Org_1 and Org_2 the vertical distances h are equal to one another ($S = 0$); in the case of Org_2 and Org_3, $h'_1 \neq h'_2 \neq h'_3$ ($S \neq 0$).

The formation of complexes containing molecules of the organic solvent was established by Rydberg[33] in a study of the extraction of thorium acetylacetonate with isobutyl methyl ketone (hexone). The curves for the distribution of thorium between hexone and the aqueous phase in the presence of acetylacetone differ from those between water and benzene or chloroform. This difference was due to the formation of complexes between $ThA_n^{(4-n)+}$ and hexone molecules (hex). Rydberg was able to calculate the equilibrium constants for the reactions:

$$ThA_2hex_4^{2+} + A^- \rightleftarrows ThA_3hex_2^+ + 2hex,$$

and

$$ThA_3hex_2^+ + A^- \rightleftarrows ThA_4 + 2hex,$$

where A^- is the acetylacetonate ion.

Thus we can always ascertain beforehand whether we are dealing only with mononuclear complexes containing no molecules of the organic solvent used. If it has been established that $m = 1$ and $S = 0$, the partition coefficient for the metal is given by

$$q = \frac{\sum_0^x \kappa_{x,N}\ \lambda_{x,N}\ [HA]^x [H]^{-N}}{\sum_0^x \sum_0^y \kappa_{x,y}\ [HA]^x [H]^{-y}}. \quad (24)$$

Eqn. (24) enables all or nearly all the constants in it to be calculated provided the type of complexes formed is known. The composition of the complexes formed in the aqueous phase is established from the relationship between $\log q$ and pH or $\log [HA][H]^{-1}$ (proportional to -pA).

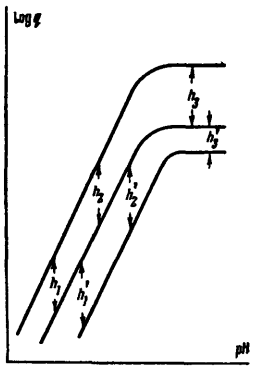


Fig. 1. Log q vs. pH for complexes with $S=0$ ($h_1 = h_2 = h_3$) and with $S \neq 0$ ($h'_1 \neq h'_2 \neq h'_3$).

As Rydberg showed, the distribution of metal between the phases varies with [H] or $[HA][H]^{-1}$ differently for various types of complexes. The curves for $\log q = f(pH)$ or $\log q = f(\log [HA][H]^{-1})$ have a different but fully determined form depending on the composition of the complex compounds in the aqueous phase. Distribution curves obtained for complexes of the types MA_n, $MA_n(OH)_p$, and $MA_n(OH)_p(HA)_r$ are shown in Fig. 2. The composition of the complexes is established experimentally by studying the distribution of the metal at several different concentrations of the reagent in the organic solvent layer (and consequently also in the aqueous phase) with other conditions the same. The descending portion of the curves at high concentrations of the ligand (shown by the broken curves) with or without a plateau may be due to the formation of negatively charged complexes. By carrying out experiments over a sufficiently wide range of HA concentrations, distribution curves can be obtained which establish unambiguously the type of complex formed.

For each type of complex appropriate formulae have been established by means of which it is possible to calculate the stability constants of the various complexes and the distribution constants of the uncharged complexes in the system under consideration. Thus for complexes of the type MA_n the equation linking the partition coefficient for the metal with the concentration of free ligand can be presented in the form

$$q = \frac{\kappa_N\ \lambda_N\ [A]^N}{\sum_0^n \kappa_n [A]^n}, \quad (25)$$

and that for complexes of the $MA_n(OH)_p$ type in the form

$$q = \frac{\sum_0^n \kappa_{n,N-n}\ \lambda_{n,N-n}\ [A]^n [OH]^{N-n}}{\sum_0^n \sum_0^p \kappa_{n,p}\ [A]^n [OH]^p}. \quad (26)$$

Many cases have been described in which the distribution of metal between the phases, in the presence of a reagent which dissociates as a monobasic acid, is represented by Eqn. (25).[41-47]

Several methods have been suggested for calculating stability constants from Eqn. (24).[48] The widely known methods of Leden[49], Bjerrum[50], Fronaeus[51], and also the

* The method suggested by Rydberg[40] for determining very large and very small partition coefficients is based on the same principle.

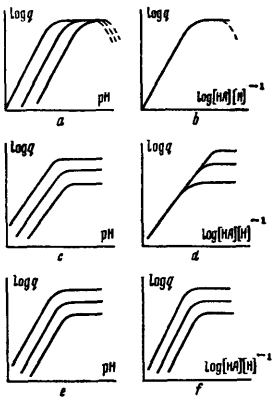


Fig. 2. Curves for the distribution of metal between the phases with $[HA]_1 > [HA]_2 > [HA]_3$ for different types of complexes: *a*), *b*) MA_n; *c*), *d*) $MA_n(OH)_p$; *e*), *f*) $MA_n(OH)_p \cdot (HA)_r$.

graphical "two-parameter" method suggested by Dyrssen and Sillén[52] can be used to calculate the characteristics of complex formation from distribution data.

Calculation of the constants in Eqn. (24) is usually carried out by methods similar to that of Leden, as follows. By introducing a series of functions of [HA], defined by the equations

$$f_\lambda = \sum_0^x \kappa_{x,N} \lambda_{x,N} [HA]^x , \quad (27)$$

$$f_y = \sum_0^x \kappa_{x,y} [HA]^x , \quad (28)$$

into Eqn. (24), we obtain the expression

$$q = \frac{f_\lambda [H]^{-N}}{\sum_0^y f_y [H]^{-y}} = \frac{f_\lambda [H]^{-N}}{f_0 + f_1 [H]^{-1} + f_2 [H]^{-2} + f_3 [H]^{-3} \ldots} \quad (29)$$

Eqn. (29) is readily put into the following form:

$$q^{-1}[H]^{-N} = P_0 = f_0 f_\lambda^{-1} + f_1 f_\lambda^{-1} [H]^{-1} + f_2 f_\lambda^{-1} [H]^{-2} + \ldots \quad (30)$$

and solved for $f_0 f_\lambda^{-1}$, $f_1 f_\lambda^{-1}$, etc. Actually the graph of $P_0 = f([H]^{-1})$ will be a curve with a limiting value $f_0 f_\lambda^{-1}$ and a limiting slope $f_1 f_\lambda^{-1}$ when $[H]^{-1}$ tends to zero:

$$\lim_{[H]^{-1} \to 0 \ (\text{or } [H] \to \infty)} P_0 = f_0 f_\lambda^{-1} + (f_1 f_\lambda^{-1} [H]^{-1} + f_2 f_\lambda^{-1} [H]^{-2} + \ldots) . \quad (31)$$

The value of $f_0 f_\lambda^{-1}$ [numerically equal to the intercept on the ordinate axis of the curve $P_0 = f([H]^{-1})$] enables us to calculate the values of the functions P_1, P_2, etc., given by Eqns. (32a) and (32b); the limiting values of these functions for $[H]^{-1} \to 0$ allow $f_1 f_\lambda^{-1}$, $f_2 f_\lambda^{-1}$, etc., to be found (e.g. $f_2 f_\lambda^{-1}$ can be obtained as the value of the limiting slope of P_1 and as the limiting value of P_2):

$$P_1 = \frac{P_0 - f_0 f_\lambda^{-1}}{[H]^{-1}} = f_1 f_\lambda^{-1} + f_2 f_\lambda^{-1} [H]^{-1} + f_3 f_\lambda^{-1} [H]^{-2} + \ldots , \quad (32a)$$

$$P_2 = \frac{P_1 - f_1 f_\lambda^{-1}}{[H]^{-1}} = f_2 f_\lambda^{-1} + f_3 f_\lambda^{-1} [H]^{-1} + \ldots . \quad (32b)$$

By successive formation of the functions P_3, P_4, etc., for different values of [HA] all the required values of $f_y f_\lambda^{-1}$ can be obtained.

According to Eqn. (28)

$$f_{y=0} = \sum_0^x \kappa_{x,0} [HA]^x = \kappa_{0,0} + \kappa_{1,0} [HA] + \kappa_{2,0} \cdot [HA]^2 + \ldots . \quad (33)$$

By definition $\kappa_{0,0} = 1$ [see Eqn. (19)]. The subsequent values of κ with $x > 0$ and $y = 0$ relate to complexes containing a metal ion M^{N+} and one or several uncharged reagent molecules but no other ligands, i.e. an addition complex $M(HA)_x^{N+}$. On the assumption that the concentration of such complexes can be neglected in comparison with that of free (hydrated) metal ions (which is true in many cases), we find that $f_0 = 1$ [Eqn. (33)]. In such a case Eqn. (34) is valid, and enables f_λ to be calculated for all concentrations of HA studied:

$$\frac{f_0}{f_\lambda} = \frac{\sum_0^x \kappa_{x,0} [HA]^x}{\sum_0^x \kappa_{x,N} \cdot \lambda_{x,N} [HA]^x} \cong \frac{1}{f_\lambda} . \quad (34)$$

Using the values of $f_0 f_\lambda^{-1}$, $f_1 f_\lambda^{-1}$, etc. obtained earlier for corresponding values of [HA] and knowing that $f_0 = 1$, it is easy to obtain the different values f_y. For example, the following expression is valid for f_1:

$$f_1 = \frac{f_1 f_\lambda^{-1}}{f_0 f_\lambda^{-1}} = \frac{f_1}{f_0} = \sum_0^x \kappa_{x,1} [HA]^x . \quad (35)$$

With the aid of f_λ and f_y, values of $\kappa_{x,N} \lambda_{x,N}$ and $\kappa_{x,y}$ are calculated, allowing the distribution constants $\lambda_{x,N}$ to be found for the various uncharged complexes.

If formation of complexes of the type $M(HA)_x^{N+}$ cannot be neglected, the calculation is greatly complicated and the accuracy of the results diminished. An approach to a solution of such a complicated expression has been suggested by Rydberg[31].

It is much simpler to calculate the stability and distribution constants for complexes of the type $MA_n^{(N-n)+}$, the general form of whose partition coefficient is given by Eqn. (25). In fact, on introducing into (25) the auxiliary constants φ_n given by (36),

$$\varphi_{N-n} = \frac{[MA_n][A]^{N-n}}{[MA_N]} = \kappa_n \kappa_N^{-1} , \quad (36)$$

Eqn. (25) is readily converted to the form

$$q = \lambda_N \left(\sum_{n=0}^{n=N} \varphi_{N-n} [A]^{n-N} \right)^{-1} , \quad (37)$$

which is convenient for the calculation of the constants appearing in it. It is not difficult to show that the equation

$$q = \frac{\lambda_N}{1 + \varphi_1 [A]^{-1} + \varphi_2 [A]^{-2} + \varphi_3 [A]^{-3} + \ldots \varphi_N [A]^{-N}} , \quad (38)$$

which is identical with (37), can be transformed into an equation for the function F_0,

$$F_0 = \frac{1}{q} = (1 + \varphi_1 [A]^{-1} + \varphi_2 [A]^{-2} + \ldots \varphi_N [A]^{-N}) \lambda_N^{-1} . \quad (39)$$

the calculation of which is quite simple. As can be seen from (39)

$$\lim_{[A]^{-1} \to 0} F_0 = \lambda_N^{-1} , \quad (40)$$

and the limiting slope is numerically equal to φ_1/λ_N. By setting up the succeeding functions F_n in a manner analogous to that used for f_y and f_λ, all the φ_n values may be calculated and with their aid all the κ_n values (and also the successive formation constants) may be found.

The calculation of stability constants from distribution data can also be carried out by utilising the concept of the mean number of ligands $\bar{n}$ per atom of metal[50]:

$$\bar{n} = \frac{\sum_{n=1}^{n} n [MA_n]_{aq}}{[M]_{\text{total aq}}} . \quad (41)$$

The fraction of the total concentration of metal occurring

in complexes of the type $MA_n^{(N-n)+}$ (n is an integral number) is expressed by the equation

$$\alpha_n = \frac{[MA_n]}{[M]_{\text{total aq}}} \quad . \tag{42}$$

As Rydberg showed[41], the relationship between $\bar{n}$ and $\log q$ is of the form

$$\bar{n} = N + \frac{d \log q}{d\,\text{pA}}, \tag{43}$$

where pA is the logarithm of the reciprocal of the concentration of free ligand [for the derivation of Eqn. (43) see p. 112]. By graphical differentiation of the distribution curve $\log q$ = f(pA)* the curve for the formation of the complex in solution, $\bar{n}$ = f(pA), is constructed by means of (43). Each point on the curve thus obtained satisfies the following equation, obtained by transformation of (41).

$$\bar{n} + (\bar{n} - 1)\kappa_1 [A] + (\bar{n} - 2)\kappa_2 [A]^2 + \ldots (\bar{n} - N)\kappa_N [A]^N = 0 \quad . \tag{44}$$

By choosing points on the curve $\bar{n}$ = f(pA) which are convenient for calculation and setting up a system of equations of the type of (44), all the values of the constants κ_n can be found. By means of the latter it is not difficult to obtain φ_n, and then also the successive formation constants k_n for the complexes in aqueous solution [see Eqn. (4)].

Apart from the above methods, the "two-parameter" method suggested by Dyrssen and Sillén[52] can be used to calculate stability and distribution constants from the distribution curves. Their graphical method** is based essentially on the assumption that the overall stability constant κ_N and the ratio of successive formation constants k_n may be represented by the following equations:

$$\kappa_N = 10^{S\,a} \quad , \tag{45a}$$

$$\frac{k_n}{k_{n+1}} = 10^{2b} \quad , \tag{45b}$$

where S is the maximum number of ligands which can add on to the metal ion and a and b are constants. Two asymptotes are drawn to the distribution curve $\log q$ = f(pA), their slopes being equal to zero and to the charge on the metal ion respectively. The value of pA at the base of the perpendicular dropped from the point of intersection of the asymptotes on to the pA axis and the distance between the distribution curve and the point of intersection of the asymptotes are used to calculate the parameters a and b by means of appropriate formulae (depending on the valency of the metal ions the factor a is to be multiplied by different whole numbers). Knowing the parameters a and b, it is easy to obtain κ_N, κ_n, and k_n. The distribution constant λ_N for the uncharged complex is numerically equal to the intercept on the $\log q$ axis of the asymptote of zero slope. If the distribution curve after reaching a maximum value (plateau) then exhibits a drop (formation of negatively charged complexes), it is possible by means of the "two-parameter" method to calculate, although with considerable error, the formation constants of some or all of the complexes having $S > N$ (in the case of univalent ligands only). The two-parameter method, giving only rough values of the stability constants (cases of systems in which k_n/k_{n+1} = const. are very rare), may be employed when it is impossible to obtain a sufficient quantity of experimental data, or if the accuracy of such data is inadequate for the independent calculation of the constants. A check of the two-parameter method on systems for which results had been calculated by other methods was carried out in several cases[44,45,52] and its suitability demonstrated for approximate calculations.

TABLE 1. Stability and distribution constants of acetylacetonates of certain actinides.

Metal	Organic solvent	log k_1	log k_2	log k_3	log k_4	log λ_N	Ionic strength of aqueous phase
Th^{4+}	C_6H_6	7.8±0.3	7.7±0.15	6.3±0.1	5.0±0.05	2.50±0.05	0.01
	$CHCl_3$	7.7±0.2	7.2±0.15	5.9±0.1	4.95±0.05	2.55±0.05	0.1
	$C_4H_9COCH_3$ (hexone)			8.0±0.15	4.3±0.15	1.5±0.1	0.1
U^{4+}	C_6H_6	8.6±0.2	8.4±0.4	6.4±0.3	6.1±0.2	3.62±0.05	0.1
	$CHCl_3$					4.0±0.2	0.1
	$C_4H_9COCH_3$					1.6±0.1	0.1
Pu^{4+}	C_6H_6	10.5±11.0	9.2±0.5	8.4±0.5	6.0±0.4	2.5±0.2	0.1
	$CHCl_3$					2.6±0.3	0.1
	$C_4H_9COCH_3$					1.4±0.1	0.1

By means of the procedures described above, many systems which form internal complexes capable of extraction by various organic solvents have been investigated. Rydberg studied the formation of complexes by acetylacetone with thorium using benzene[41], chloroform[43], and other solvents[32,33]. He studied also the formation of complexes by uranium(IV),[45] plutonium*[44], lanthanum, samarium, hafnium, and other elements[58] with this reagent. In the majority of cases mononuclear complexes of the type $MA_n^{(N-n)+}$, containing no organic solvent molecules in their composition, were formed in the aqueous phase. Eqn. (37) is applicable to this type of complex. Calculations on such systems were carried out mainly by Leden's method, more rarely by Bjerrum's method, and only in exceptional cases by the Dyrssen–Sillen two-parameter method. It is noteworthy that Rydberg was able to study the stability of compounds of quadrivalent uranium, the ready oxidation of which to the sexivalent state has frequently hindered the employment of other methods.

Values of the successive formation constants of the acetylacetonato complexes of Th^{4+}, U^{4+}, and Pu^{4+} and the distribution constants of the uncharged complexes λ_N found by Rydberg and his coworkers for various solvent systems are given in Table 1.[12]

In the case of the acetylacetonato complexes of sexivalent uranium the distribution of metal between the phases cannot be represented by Eqn. (37). As Rydberg showed, complexes of the general type $M(HA)_x(H)_{-y}$ are formed in this case. By appropriate treatment of the distribution curves

* Graphical differentiation of the curve is conveniently carried out by means of a special instrument designed by Chmutov[53,54]. For methods of graphical differentiation see the books cited in the next two references[55,56].

** The reader is advised to consult ref. 52, pp. 665–674 (Ed. of Translation).

* The distribution of Pu(IV) between an aqueous phase and benzene has also been studied by Harvey[57], but not with the aim of determining the stability of the complexes formed.

Rydberg was able to calculate the equilibrium constants of the following reactions:

$$UO_2^{2+} + OH^- \rightleftarrows UO_2OH^+ \qquad K_{eq} = 10^{9.6},$$
$$UO_2^{2+} + 2OH^- \rightleftarrows UO_2(OH)_2 \qquad K_{eq} = 10^{18.2},$$
$$UO_2^{2+} + OH^- + A^- \rightleftarrows UO_2AOH \qquad K_{eq} = 10^{15.6},$$
$$UO_2^{2+} + A^- \rightleftarrows UO_2A^+ \qquad K_{eq} = 10^{6.8},$$
$$UO_2^{2+} + A^- + HA \rightleftarrows UO_2AHA^+ \qquad K_{eq} = 10^{8.7},$$
$$UO_2^{2+} + 2A^- \rightleftarrows UO_2A_2 \qquad K_{eq} = 10^{13.1},$$
$$UO_2^{2+} + 2A^- + HA \rightleftarrows UO_2A_2HA \qquad K_{eq} = 10^{14.8},$$
$$UO_2^{2+} + HA \rightleftarrows UO_2HA^{2+} \qquad K_{eq} < 1,$$
$$UO_2^{2+} + 2HA \rightleftarrows UO_2(HA)_2^{2+} \qquad K_{eq} < 10,$$
$$UO_2^{2+} + 3HA \rightleftarrows UO_2(HA)_3^{2+} \qquad K_{eq} < 100,$$
$$(UO_2A_2)_{aq} \rightleftarrows (UO_2A_2)_{CHCl_3} \qquad K_{part} = 3.3,$$
$$(UO_2A_2HA)_{aq} \rightleftarrows (UO_2A_2HA)_{CHCl_3} \qquad K_{part} = 22.$$

As was noted earlier (p. 104 etc.), if the complexes formed in the aqueous phase do not include any solvent in their composition, their stability constants are independent, within the limits of experimental error, of which solvent is used in the investigation. This is fully confirmed in the case of the acetylacetonatothorium complexes (see Table 1).

It is interesting to compare data obtained by the distribution method with the results of a study of the stability of the same complex compounds by other, e.g. potentiometric, methods. Izatt, Fernelius, and their coworkers[59-67] carried out a major investigation of the complexes of acetylacetone and other β-diketones with various metals. They determined in particular the formation constants of the acetylacetonato complexes of thorium and uranium(VI) in aqueous solution. Comparison of the data of Rydberg[33,41] with those of Izatt[66] shows that both methods — distribution and potentiometric — give very similar results. The fourth formation constant of acetylacetonatothorium is an exception. In Izatt's experiments this constant was calculated from data obtained at quite high pH values, at which the effect of hydrolysis of the metal ions is most evident. Rydberg, using the data of Hietanen[68] on the hydrolysis of thorium ions, established that a considerably greater proportion of the thorium ions were hydrolysed in Izatt's experiments than in the distribution experiments* (the concentration of thorium ions in the aqueous phase after equilibrium had been reached with the organic phase was about 10^5 times as great in Izatt's experiments as in Rydberg's). Rydberg[12] obtained a thermodynamic formation constant of $\log k_4 = 5.1$, which is more likely to be correct than Izatt's value.

Izatt, Fernelius, and Block found the thermodynamic formation constants of the acetylacetonatouranyl complexes UO_2A^+ and UO_2A_2 to be $10^{7.7}$ and $10^{6.4}$ respectively. Applying the necessary corrections for the activity coefficients in 0.1 M $NaClO_4$ solutions, Rydberg[12] obtained values of $\sim 10^{7.1}$ and $\sim 10^{13.6}$ for the analogous constants (see above). Thus, although the former value shows satisfactory agreement with Izatt's data, a considerable difference is observed with the latter constant. Such a divergence in the results may be caused by insufficient variation of the acetylacetone concentration by Izatt and his coworkers. This would probably not allow him to detect other complexes formed between UO_2^{2+} and acetylacetonate ions (e.g. UO_2A_2HA, etc. — see above), and this would produce an error in the determination of the constants.

* For the mechanism of the hydrolysis of quadrivalent thorium, uranium, and other actinides, see e.g. refs. 69-72.

On the basis of the results of the study of the acetylacetone complexes of actinides by the distribution method[12] Rydberg concluded that the formation constants for quadrivalent Th, U, and Pu increase as the ionic radius decreases. He was not able to detect any direct relationship between the distribution constants for the uncharged complex in the organic and aqueous phases and the stability constants of the complexes (or radii of the metal ions). Nor did he observe any direct relationship between the distribution constant for the reagent HA and that for the corresponding uncharged complex MA_N with a given solvent. In Rydberg's opinion this shows that some caution is necessary in comparing distribution data with data on the stability of internal complexes. However, in investigations of several reagents of one and the same class a definite relationship is sometimes observed between the distribution constants of the reagent and of the complex compounds formed by it[73-75].

Apart from the acetylacetone complexes, a number of complex compounds of thenoyltrifluoroacetone, widely used in practice for the separation, purification, and study of various elements, were investigated[76-82]. Huffman et al.[82], studying the possibility of separating zirconium and hafnium by means of various fluorinated β-diketones, showed that in 2 M perchloric-acid solution the species containing Zr(IV) and Hf(IV) are mainly monomers, the formation of which can be represented by the equation:

$$M^{4+} + 4HA \rightleftarrows MA_4 + 4H^+.$$

The equilibrium constant for the extraction process at constant hydrogen-ion concentration is represented by the equation

$$\log K_{eq} = \log q - 4 \log [HA], \qquad (46)$$

where $q = [MA_4]_{org}/\Sigma[M]$, and [HA] is the activity of the β-diketone in the organic phase.

They established that the $\log q = f(\log [HA])$ curves for different solvents have the same slope, equal to 4, and that when complexes are formed between isovaleroyltrifluoroacetone and Zr or Hf the distribution constants of the corresponding compounds in the n-hexane–H_2O system are higher than those for the benzene–H_2O system, whereas the converse holds for the reagent itself. An equation analogous to (46) was obtained by Keenan and Suttle[76] in a study of complex formation between praseodymium and thenoyltrifluoroacetone. They plotted the graph of $\log q = f(pH)$ and calculated its slope by the method of least squares, obtaining values of 2.96 and 2.93 for different reagent concentrations (the composition of the complex is thus PrA_3). The preparation of complex compounds of 2-furoyltrifluoroacetone, benzoylacetone, and dibenzoylmethane with thorium, uranium(IV), samarium, and other elements, has been described[83-86], but, as far as we know, their physicochemical characteristics have so far been little studied.

A large amount of work using the above methods has also been carried out on the formation of complexes between actinides and organic reagents important in analytical chemistry. Thus Dyrssen investigated complex formation between thorium, lanthanum, yttrium, and uranium and tropolone[87], cupferron[42], 1-nitroso-2-naphthol and 2-nitroso-1-naphthol[88], and 5,7-dihalogenated derivatives of hydroxyquinoline[89]. In addition, a study was made of the stability of compounds of samarium, lanthanum, hafnium, strontium, and other elements with several of these reagents[90-92]. Hök-Bernstrom and Dyrssen investigated the formation of complexes of thorium, uranium(VI), and in

TABLE 2. Composition of complex compounds of certain actinides established by the distribution method.

System			Type of complex		Reference
M	HA	Org	aqueous phase	organic phase	
Th^{4+}	acetylacetone	C_6H_6 / $CHCl_3$	$MA_n^{(4-n)+}$	MA_N	33
Th^{4+}	"	hexone	$MA_n(Org)_s$	MA_N	33
U(VI)	"	C_6H_6 / $CHCl_3$ / hexone	$MA_n(OH)_p$ / $MA_n(HA)_r$	$MA_N(HA)_r$	33
U^{4+}	"	C_6H_6	$MA_n^{(4-n)+}$	MA_N	45
U(VI)	salicylic acid	hexone	$MA_n(OH)_p$	$MA_N(HA)_r$	94
Th^{4+}	"	"	$MA_n^{(4-n)+}$	$MA_N(HA)_r$	93
U(VI)	methoxybenzoic acid	"	$MA_n(OH)_p$	MA_N	94
Th^{4+}	"	" / $CHCl_3$	$MA_n^{(4-n)+}$	MA_N	93

certain cases tervalent lanthanum with salicylic, methoxybenzoic, cinnamic, *N*-phenylbenzohydroxamic, and other benzene carboxylic acids [93-97]. Table 2 shows the results of a study of the composition of some of these complex compounds in various solvent systems.

On the basis of the results obtained Dyrssen discussed the influence of the structure of the organic reagent on the stability of its complex compounds with metals [98]; he also worked out methods for separating and determining certain elements [99].

The values of the successive stability constants of complex compounds make it possible to calculate the percentage distribution of the metal between complexes of differing composition and the mole fractions of the latter as functions of the concentration of free ligand (see p. 106). Curves of this type are given in a number of papers [41,47].

As can be seen from the above account, with any method of treating the experimental results it is necessary to know the functional dependence of the partition coefficient of the metal on the concentration of free ligand. Calculation of the latter is impossible without a preliminary detailed investigation of the reagent under the given experimental conditions. If the concentrations of metal ions and ligand are similar, it is necessary to take into account the decrease in concentration of the ligand due to complex formation. This always complicates the calculations, and therefore it is much more convenient to work with sufficient excess of reagent to make this decrease negligible. This is quite possible when radioactive isotopes are used. The distribution of metal between the phases can then be measured at extremely low concentrations of metal ions, which allows not only the amount of ligand combined in the complexes to be neglected but also the range of experimental concentrations to be considerably widened with far less risk of polymerisation or of exceeding the solubility products of the compounds under investigation.

The preliminary investigation of the reagent consists in effect in the determination of its dissociation constants (for acid dissociation in the overwhelming majority of cases) and the distribution constants between the aqueous phase and a few — at least two — organic solvents at a given ionic strength and temperature. The dissociation constant of the reagent can be determined spectrophotometrically, potentiometrically, by a two-phase titration method, etc. [100-109]. The distribution constants of the reagent in several two-phase systems (organic solvents which are subsequently to be used in the study of complex formation are chosen) are determined at various concentrations of the reagent in the organic-solvent layer, covering a sufficiently wide range. If the distribution constant is practically constant for different concentrations of the reagent, it may be accepted that the reagent does not undergo molecular association in the organic layer, or in other words that the molecular weight of the reagent is the same in the two phases*. Possible association of the reagent molecules in the organic phase may also be detected spectrophotometrically [112,113]. In the absence of any polymerisation of the reagent in either phase, the concentration of free ligand in an aqueous solution of a definite low and constant ionic strength is calculated from the equation

$$pA = pK_{diss\,HA} + \log[H] - \log[HA]^{\circ}_{org} + \log(K_{part\,HA}+1 + K_{diss\,HA}[H]^{-1}), \quad (47)$$

where pA = -log [A], $pK_{diss\,HA}$ is the logarithm of the reciprocal of the dissociation constant and $K_{part\,HA}$ is the distribution constant of the reagent, both at given ionic strength and temperature, $[HA]^{\circ}_{org}$ is the concentration of the reagent in the original solution (in the organic solvent used), and [H] is the hydrogen-ion concentration under equilibrium conditions. If the phases have different volumes, appropriate correction factors are introduced into Eqn. (47). When such solvents as C_6H_6, $CHCl_3$, and certain others are used, the changes in volume undergone by the phases on prolonged shaking are insignificant and can be neglected [33,44].

In certain cases the phenomenon of keto-enol tautomerism must be taken into account in calculating the concentration of the ligand in the aqueous phase. It is known, for example, that β-diketones exist in aqueous solution in two forms, the keto form and the enol form. The latter dissociates, splitting off a hydrogen ion and forming an anion which can add on to various metal ions to form internal complexes. Many workers have investigated the keto-enol tautomerism of β-diketones [114-117]. Rydberg [101] determined the keto-enol tautomerism constant for acetylacetone and the distribution constants of its keto and enol forms in the benzene-water system. (The distribution constant for acetylacetone between benzene and water according to Rydberg is 5.95 ± 0.05 over the pH range 1-7.) The acid dissociation constant of acetylacetone and other β-diketones determined in the usual way [Eqn. (1)] will contain a certain error if the concentration of the enol form is taken as equal to the total concentration of the reagent. Frequently, however, this error is insignificant. As Calvin and Wilson [118] remark: "The K_{diss} as written here (see p. 101) represents a characteristic of the acid strength of the enol form as such. This, however, is not quite the constant which we have measured and called K_{diss}. The measured value represents the apparent dissociation constant and includes the constant for the keto-enol tautomerism in the following manner:

$$K_{enol} = K_{appar}\ (1 + K_1),$$

where K_1 = [keto]/[enol]. It is clear that for aromatic compounds $K_1 \cong 0$, so that $K_{enol} \cong K_{appar} = K_{diss}$. For the aliphatic compounds, however, K_1 will have an appreciable

* For methods of studying association equilibria of organic molecules in organic solvents by the distribution method see e.g. refs. 110 and 111.

value, thus making K_{diss} for these compounds a lower limit for the acidity of the enol". The correction for K_1 will hardly affect the results in the case of acetylacetone and similar reagents, and therefore many authors in their calculations employ values of the dissociation constants of β-diketones without any correction for K_1. The acid dissociation constant of acetylacetone was also determined by Eidinoff[119], and the distribution of the reagent between $CHCl_3$ and aqueous solutions of perchloric acid was studied by Salvinien[120]. The latter found the distribution constant of acetylacetone in the system to fall from 23.7 to 10.2 with increase in the $HClO_4$ concentration from 0 to 1.94 M. In the water – CCl_4 system the distribution constant diminishes from 3.3 to 1.4. In general, the results obtained by Salvinien are in satisfactory agreement with Rydberg's data[106].

The distribution method has been successfully used to investigate hydrolysis and polymerisation reactions occurring in aqueous solutions of metal ions. Here we should first consider, perhaps, the study of the chemistry of aqueous solutions of zirconium. The great difficulties caused by the extreme readiness with which this element is hydrolysed make it understandable why, until very recently, nothing definite was known about the state of Zr(IV) in aqueous solution. The earlier results indicated the formation of polynuclear complexes[121], but the composition of the latter could not be regarded as reliably established. In recent years Connick, Reas, and other authors[121-128] have carried out a series of investigations with the aim of establishing the composition and in some cases the stability of the zirconium-containing complexes formed in solutions of perchloric and other acids. The nature of this element compelled these workers to pay more attention to complexes of mixed type $MA_n(OH)_p$ than had hitherto been done by other investigators[10,14]. By studying the distribution of Zr(IV) between aqueous perchloric acid and benzene in the presence of thenoyltrifluoroacetone, Connick, Zielen, and others attempted to establish the composition of the complex compounds extracted and of the zirconium-containing species present in the aqueous phase, and also to determine the characteristics of the process of complex formation by Zr(IV) with the majority of the most frequently encountered anions. The usual methods of investigating the composition of complexes in solution (potentiometric, spectrophotometric, solubility measurement, freezing-point determination, etc.) would not, in the view of the above authors, yield reliable results owing to the great tendency of Zr(IV) to hydrolysis even in very acid solutions. They therefore chose a method based on the distribution equilibria of zirconium between the aqueous phase to be investigated and an organic solvent containing the complex-forming reagent.

In the aqueous phase zirconium forms complexes with thenoyltrifluoroacetone to an insignificant extent, but the internal complex formed dissolves readily in the organic solvent (benzene, chloroform, etc.) and is in equilibrium with all the species in the aqueous phase. Thus any change in the complex formation in the aqueous solution should be quantitatively reflected in the passage of metal into the organic – solvent layer. Connick and McVey[124], with the aim of establishing the composition of the complex which is extracted, studied first of all the variation of the partition coefficient of the metal with thenoyltrifluoroacetone concentration for a constant hydrogen-ion concentration in the aqueous phase. Using a solvent of low dielectric constant (benzene) and assuming that only neutral, uncharged particles pass into the organic solvent layer (similarly as was done later by Rydberg[31-33] and other Scandinavian investigators) Connick and his coworkers examined the process represented by the equation

$$Zr(OH)_nA_m^{(4-n-m)+} + (p-m)HA \rightleftarrows Zr(OH)_{4-p}A_p + (4-m-n)H^+ + (n+p-4)H_2O, \quad (48)$$

the equilibrium constant of which is

$$K_{eq\ m,n,p} = \frac{[Zr(OH)_{4-p}A_p][H^+]^{4-m-n}[H_2O]^{n+p-4}}{[Zr(OH)_nA_m^{(4-n-m)+}][HA]^{p-m}}. \quad (49)$$

(A represents the thenoyltrifluoroacetonate ion.) By means of (49) and certain transformations we can obtain an equation relating the partition coefficient to the reagent concentration and other parameters of the system*:

$$\frac{\partial \ln q}{\partial \ln [HA]} = -4f_0 - 3f_1 - 2f_2 - f_3 + 4f_0' + 3f_1' + 2f_2' + f_3', \quad (50)$$

where f_n is the fraction of the total metal concentration in complexes with a definite number of ligands (thenoyltrifluoroacetonate or hydroxyl ions). By measuring the slope of the curve for $\log q$ plotted against $\log [HA]$ it is possible to obtain the number of ligands combined with Zr(IV) in the extracted complex and in all the complexes in the aqueous phase. By means of the distribution method Connick and other investigators have obtained the degree of polymerisation as a function of the variables of the system (concentration of metal ions, acidity of solution, etc.), and have calculated the equilibrium constants of the successive polymerisation processes. The results obtained for analogous systems by other methods (spectrophotometric, chromatographic, etc.)[129-132] are fundamentally in agreement with those obtained by the distribution method. Certain divergencies (e.g. in the degree of polymerisation or the existence of the unhydrolysed ion Zr^{4+}) are perhaps due to different experimental conditions (ionic strength of the solution, difference in properties of the individual mineral acids, etc.).

The work of Connick and his coworkers has established the possibility of using the distribution method to determine the composition and stability of complexes which are not extracted by solvents of low dielectric constant. This is done by adding a secondary ligand (HSO_4^-, F^-, and certain other anions) to a two-phase system containing water, organic solvent, metal ions, and an organic reagent giving on dissociation the primary ligands which form a complex readily extracted by the organic solvent used. The relationship found between the partition coefficient of the metal and the concentration of the secondary ligand gives an indication of the composition of the complexes in the aqueous solution, and in certain cases makes possible a quantitative treatment of the complex formation between the metal ions and the secondary ligand. This procedure (introduction of a secondary ligand) substantially widens the possibilities of the distribution method and suggests that it will prove very effective in many cases for the investigation of other systems, including both extractable and non-extractable complex compounds. This method has been used to study the formation of complexes by Th(IV) with iodate ions[133], the anions of various monobasic acids (HCl, HF, HNO_3, $HClO_3$, $HBrO_3$, $ClCH_2COOH$, and HCOOH), and other ligands[134-136]. Day and Stoughton[135] thus demonstrated the existence in the aqueous phase of mixed complexes of the type $Th(NO_3)F^{2+}$

* The reader is advised to consult ref. 124, p. 3184 (Ed. of Translation).

and $Th(NO_3)F_2^+$, and calculated the equilibrium constants for the following reactions (ionic strength $I = 0.5$):

$$Th^{4+} + HF \rightleftarrows ThF^{3+} + H^+ \qquad K_{eq} = 4.3 \cdot 10^4,$$
$$Th^{4+} + 2HF \rightleftarrows ThF_2^{2+} + 2H^+ \qquad K_{eq} = 3.1 \cdot 10^7,$$
$$Th^{4+} + IO_3^- \rightleftarrows Th(IO_3)^{3+} \qquad K_{eq} = 7.6 \cdot 10^2,$$
$$Th^{4+} + 2IO_3^- \rightleftarrows Th(IO_3)_2^{2+} \qquad K_{eq} = 6.2 \cdot 10^4,$$
$$Th^{4+} + 3IO_3^- \rightleftarrows Th(IO_3)_3^+ \qquad K_{eq} = 1.4 \cdot 10^7,$$
$$Th^{4+} + BrO_3^- \rightleftarrows Th(BrO_3)^{3+} \qquad K_{eq} = 6.4,$$
$$Th^{4+} + 2BrO_3^- \rightleftarrows Th(BrO_3)_2^{2+} \qquad K_{eq} = 8.2,$$
$$Th^{4+} + ClO_3^- \rightleftarrows Th(ClO_3)^{3+} \qquad K_{eq} = 1.84,$$
$$Th^{4+} + NO_3^- \rightleftarrows Th(NO_3)^{3+} \qquad K_{eq} = 4.73,$$
$$Th^{4+} + Cl^- \rightleftarrows ThCl^{3+} \qquad K_{eq} = 1.76,$$
$$Th^{4+} + ClCH_2COOH \rightleftarrows Th(ClCH_2COO)^{3+} + H^+ \qquad K_{eq} = 1.33,$$
$$Th^{4+} + Cl_2CHCOOH \rightleftarrows Th(Cl_2CHCOO)^{3+} + H^+ \qquad K_{eq} = 5.74,$$
$$Th^{4+} + 2Cl_2CHCOOH \rightleftarrows Th(Cl_2CHCOO)_2^{2+} + 2H^+ \qquad K_{eq} = 12.7,$$
$$Th^{4+} + CCl_3COOH \rightleftarrows Th(CCl_3COO)^{3+} + H^+ \qquad K_{eq} = 8.23,$$
$$Th^{4} + 2CCl_3COOH \rightleftarrows Th(CCl_3COO)_2^{2+} + 2H^+ \qquad K_{eq} = 26.7.$$

Rossotti and Rossotti[137] investigated the hydrolysis of In^{3+}. They established the existence of the hydroxo complexes $In(OH)^{2+}$ and $In(OH)_2^+$, and calculated their formation constants. Their results are in good agreement with the potentiometric data of Biedermann for an analogous system* [138].

Allen[141] studied the sulphate complexes of UO_2^{2+} by the above method of introducing a secondary ligand, and Betts and Leigh[142] used the same method to study complex formation between U(IV) and HSO_4^-. The latter detected the complexes $U(SO_4)^{2+}$ and $U(SO_4)_2$, with formation constants of 338 and 0.74 respectively**.

Connick, Reas, and their coworkers investigated only zirconium compounds. The theory of the distribution method has been more widely developed in recent years by a group of English investigators led by Irving. In a series of papers Irving, Williams, Rossotti, and others have considered the general form of the distribution law for a metal distributed between organic and aqueous phases, and have described the application of their results to the investigation of a number of systems[137,144-153]. Irving and his collaborators have considered the case of non-ideal systems and their proposed methods for interpreting the results are therefore somewhat more general than those described by Rydberg and others. The main theoretical arguments of Irving and his coworkers are briefly examined below.

Irving has considered both ideal and non-ideal systems. By the former are understood systems in which wide variation in the experimental conditions produces no changes in the properties of either solvent, and in which the degree of solvation (by water or organic solvent molecules) of any species remains unchanged in either phase. In other words, in ideal systems the average numbers of water and organic solvent molecules associated with each species are constant, as are also the stability constants and partition coefficients. In non-ideal systems a change in one or more variables (concentrations of hydrogen ions, metal ions, reagent, and ligand) produces changes in the composition of both phases (the mutual miscibility of the solvents changes), and consequently the partition coefficients, stability "constants", etc., are no longer constant.

Irving[144] divides all the types of extracted compounds into the following four main classes: (1) covalent compounds of the type of SO_2, Cl_2, OsO_4, etc.; (2) internal complexes of metals with organic reagents (dithizone, acetylacetone, dimethylglyoxime, etc.); (3) mineral acids and their salts and acido complexes (e.g. $HFeCl_4$, etc.); and (4) certain salts containing bulky anions or cations (e.g. the compound of Fe(II) tri-1,10-phenanthrolinate with alkylsulphonates or alkyl sulphates, etc.) [154,155]. Extraction of compounds of the first type is readily explained on the basis of Nernst's theory[6]. The interpretation of the extraction results for compounds of the fourth type is basically similar to that for internal complexes. The greatest differences in behaviour on partition in two-phase systems are observed with compounds of the second and third types, namely, internal complexes and complexes with inorganic ligands.

In the case of internal complexes a quite stable unsolvated monomeric complex MA_n is formed at such a low concentration of the ligand A^- that the properties of the aqueous phase as a solvent remain practically unchanged. Internal complexes which are very sparingly soluble in water are at the same time, as a rule, readily soluble in non-polar organic solvents (benzene, chloroform, carbon tetrachloride, etc.). The organic reagent HA, the anion of which is a ligand in MA_n, also dissolves well in the same organic solvents. Addition of foreign ions to the aqueous phase and the resulting change in composition do not affect the composition of the (usually neutral) species which is extracted, and the absence of hydration in the extracted complexes eliminates the possibility of any change in the composition of the organic phase. Thus the mutual miscibility of two phases is practically unchanged even when the concentration of HA and A^- is varied over a wide range in order to obtain partition coefficients which are more convenient to measure. In such a case the stability constants of the complexes in the aqueous solution, and also the distribution constants of the extracted species, will be constant provided that the ionic strength of the aqueous phase is kept constant, and their values can be obtained by carrying out a sufficiently large number of experiments. In other words, the system is "ideal", and when different solvents are employed the $\log q = f(pA)$ curves will be parallel to one another (see p. 104). Parallel curves will not be obtained if the solvation in the different organic solvents is different.

In the extraction of compounds of the third type, strongly hydrated species may pass into the organic layer, causing considerable changes in composition of both phases. Besides, two or more complex species may be extracted together instead of one extracted with compounds of the second class. Such a marked change in composition of the phases may lead to a change in the values of the stability and distribution constants, or may cause the system to diverge from ideal behaviour. In certain cases this may be avoided by appropriate choice of organic solvent or of the other components of the system[146,147]. The maintenance of a constant ionic strength in the organic phase would considerably diminish such complications, but up to now control of the ionic strength in an organic solvent has hardly been possible in the study of the distribution of acido complexes and inorganic salts in two-phase systems. The extraction of an uncharged internal complex takes place at an insignificant total concentration, and therefore cannot produce any appreciable change in the activity coefficients

* For the hydrolysis of In^{3+} in aqueous solution see also refs. 139, 140, etc.

** For complex formation between U(VI) and SO_4^{2-} see, for example, ref. 143.

in either phase. Addition of a neutral salt to the aqueous solution to keep the ionic strength constant during extraction of compounds of the third type can markedly change the behaviour of the system, and this also distinguishes systems of the third and second types from one another. Apart from this the partition coefficient for the extraction of internal complexes is frequently independent of the concentration of metal ions (over a certain range of concentrations), but in the case of acido complexes it may increase, decrease, or remain constant depending on the nature of the extracted species.

The above complications occurring in the extraction of inorganic salts and acido complexes were taken into account by Irving and his coworkers in working out a general method for interpreting distribution data. Their analysis of complex formation using extraction techniques was based on a combination of Bjerrum's concept of a stepwise mechanism of complex formation[156] and Nernst's distribution law[6]. Irving first considered the equilibria between simple ions and all the complex species in a system containing two immiscible solvents. Such equilibria are quantitatively described by the successive formation constants which determine the relative concentrations of various complexes in aqueous solutions, and a series of distribution constants for such complexes in the two-phase system under examination. Irving et al. did not consider the possibility of a stepwise equilibrium between the extracted complexes in the organic phase, since it is not possible to establish from distribution data whether a particular complex found in the organic layer has migrated from the aqueous phase or whether it has been formed in the organic phase from components in distribution equilibrium with similar components in the aqueous solution.

Assuming that, in the aqueous phase saturated with organic solvent (Org) and containing metal ions M, hydrogen ions H^+, and ligand A^-, the concentration of the acid and the anion A^- is such that hydrolysis of any cation can be neglected, all the complexes of type MA_n, acido complexes H_hMA_n, polynuclear molecules M_2A_6, $H_2M_3A_{12}$, etc., in equilibrium with one another can be represented as a complex of the general type (IV):

$$H_hM_mA_n(H_2O)_p(Org)_s .$$

The concentration of type IV complexes is determined by their stability constants κ:

$$\kappa_{h,m,n,p,s} = \frac{[H_hM_mA_n(H_2O)_p(Org)_s]}{[H]^h[M]^m[A]^n[H_2O]^p[Org]^s}, \quad (51)$$

and the distribution in the two-phase system by the distribution constant:

$$\gamma_{h,m,n,p,s} = \frac{[H_hM_mA_n(H_2O)_p(Org)_s]_{org}}{[H_hM_mA_n(H_2O)_p(Org)_s]_{aq}}. \quad (52)$$

The partition coefficient of the metal between the phases, numerically equal to the ratio of the total concentrations of all forms of metal-containing complexes in the organic and in the aqueous phases, can be represented as follows:

$$q = \frac{\sum m[H_hM_mA_n(H_2O)_p(Org)_s]_{org}}{\sum m[H_hM_mA_n(H_2O)_p(Org)_s]_{aq}} = \quad (53)$$

$$\frac{\sum \gamma_{h,m,n,p,s}\ \kappa_{h,m,n,p,s}\ m[H]^h[M]^m[A]^n[H_2O]^p[Org]^s}{\sum \kappa_{h,m,n,p,s}\ m\ [H]^h[M]^m[A]^n[H_2O]^p[Org]^s}.$$

Eqn. (53) differs from (20) in that its numerator contains the distribution constants of all the species distributed between the phases instead of the distribution constant of the uncharged complex $\lambda_{m,x,mN,s}$ in Eqn. (20). The mean composition of the complexes in the organic and aqueous phases may not be the same. Using the concept of a mean number $\bar{E}$ of metal atoms per complex molecule in the organic phase and the corresponding mean $\bar{\epsilon}$ in the aqueous solution, and applying similar concepts to the mean numbers of hydrogen ions, ligand ions, water molecules, and organic solvent molecules per atom of metal, Irving put forward an expression for q in the form

$$q = \frac{\bar{\theta}\bar{E}\bar{B}[H]^{\bar{E}\bar{H}}[M]^{\bar{E}}[A]^{\bar{E}\bar{N}}[H_2O]^{\bar{E}\bar{P}}[Org]^{\bar{E}\bar{S}}}{\bar{\kappa}^{\bar{\epsilon}}[H]^{\bar{\epsilon}\bar{h}}[M]^{\bar{\epsilon}}[A]^{\bar{\epsilon}\bar{n}}[H_2O]^{\bar{\epsilon}\bar{p}}[Org]^{\bar{\epsilon}\bar{s}}}, \quad (53a)$$

where $\bar{H}$ and $\bar{h}$ are the mean numbers of hydrogen ions, $\bar{N}$ and $\bar{n}$ are the mean numbers of ligands, $\bar{P}$ and $\bar{p}$ are the mean numbers of water molecules, and $\bar{S}$ and $\bar{s}$ are the mean numbers of organic solvent molecules, per atom of metal in the averaged complex molecule in organic and aqueous phases: correspondingly $\bar{\theta}$ and $\bar{B}$ are the distribution and stability constants of the averaged complex molecule in the organic phase, and $\bar{\kappa}$ is the stability constant of the averaged complex molecule in the aqueous phase. On taking logarithms, (53a) readily yields the expression

$$\log q = \log\left(\frac{\bar{\theta}\bar{B}}{\bar{\kappa}}\right) + \log\left(\frac{\bar{E}}{\bar{\epsilon}}\right) + (\bar{E}\bar{H} - \bar{\epsilon}\bar{h})\log[H] + (\bar{E} - \bar{\epsilon})\log[M] + (\bar{E}\bar{N} - \bar{\epsilon}\bar{n})\log[A] + (\bar{E}\bar{P} - \bar{\epsilon}\bar{p})\log[H_2O] + (\bar{E}\bar{S} - \bar{\epsilon}\bar{s})\log[Org] \quad (53b)$$

In ideal systems the stability constants of the averaged complexes in the organic and the aqueous phases, $\bar{B}$ and $\bar{\kappa}$, the distribution constant of the averaged complex in the organic phase $\bar{\theta}$, and also the indices $\bar{P}$, $\bar{p}$, $\bar{S}$, and $\bar{s}$ are constant. With constant ionic strength in the aqueous phase, the mutual solubility of the solvents is constant, and expression (53b) may be written in the form

$$\log q = \Psi + \log\left(\frac{\bar{E}}{\bar{\epsilon}}\right) + (\bar{E}\bar{H} - \bar{\epsilon}\bar{h})\log[H] + (\bar{E} - \bar{\epsilon})\log[M] + (\bar{E}\bar{N} - \bar{\epsilon}\bar{n})\log[A], \quad (54)$$

where Ψ is a constant independent of [M], [H], and [A]. With the help of Eqn. (54) it is possible to draw definite conclusions as to the composition of the various complexes existing in the organic and aqueous phases, and it is also possible, if a sufficient number of measurements are made, to calculate the values of the constants which it contains.

To find the mean number of metal atoms per averaged complex molecule, the so-called "polymerisation factor"[144], Eqn. (54) is differentiated with respect to the concentration of metal ions at constant concentrations of ligand and hydrogen ions. It is easy to show that

$$\left(\frac{\partial \log q}{\partial \log[M]}\right)_{[H],[A]} = (\bar{E} - \bar{\epsilon}) . \quad (55)$$

Thus if the value of the partial derivative (55) is found to be zero, the degree of polymerisation of the metal-containing complexes is the same in each phase. In the limiting case, when the concentration [M] tends to zero, the values of E and ϵ tend to unity: i.e. at very low concentrations of metal ions only mononuclear complexes are formed in organic and aqueous phases. This has been established for the majority of metals, the only possible exception being elements that are extremely readily hydrolysed. It is also obvious that, if $(\partial \log q/\partial \log[M])_{[H],[A]} > > 0$, the degree of polymerisation in the organic phase is higher than in the aqueous phase, and conversely if the value of this derivative is less than zero. By means of Eqn. (55) it is possible to obtain information as to the relative polymerisation of the complexes in each of the phases,

but, as noted above, it is impossible to judge the nature of the species undergoing such polymerisation in the organic phase. Relationships of the type (55) were investigated in particular by Connick and Reas in their work on the polymerisation of zirconium in aqueous solution[125]. All the cases covered by Eqn. (55) have been described in the literature. Thus the condition $\bar{E} = \bar{\varepsilon}$ is achieved in practice in the extraction of internal complexes[31-33], and cases of association of the extracted molecules in the organic phase have been established in a study of the extraction of halide complexes of iron, gold, and other elements[157,158]. The formation of dimers in the aqueous phase ($\bar{\varepsilon} > \bar{E}$) has been observed by Irving and Rossetti in the extraction of In^{3+} from hydrobromic acid solutions[147].

The difference in the mean number of ligands associated with each complex-forming metal atom in the averaged complexes in each phase is indicated by the value of the partial derivative of the partition coefficient with respect to the ligand concentration for [M] = const. and [H] = const.:

$$\left(\frac{\partial \log q}{\partial \log [A]}\right)_{[H][M]} = \bar{E}\bar{N} - \bar{\varepsilon}\bar{n} \quad . \qquad (56)$$

What has been said about Eqn. (55) is applicable also to (56). The value of the derivative obtained indicates either the same or different mean numbers of ligands in each averaged complex in organic and aqueous phases. If mononuclear complexes are formed, $\bar{E} = \bar{\varepsilon} = 1$, and Eqn. (56) may be written in the form:

$$\left(\frac{\partial \log q}{\partial \log [A]}\right)_{[H],[M]} = \bar{N} - \bar{n} \quad . \qquad (57)$$

If it is established that a single neutral complex is transferred to the organic solvent layer (such a case usually occurs in the extraction of internal complexes by non-polar solvents), Eqn. (57) can be used to find all the stability constants of the complex compounds formed in the aqueous phase. A similar equation was deduced by Rydberg for the particular case of the distribution of acetylacetonato complexes of thorium between benzene and an aqueous phase[41]. The formation of compounds $ThA_n^{(4-n)+}$, was established in the latter system, the extracted complex having $\bar{N} = 4$ (p. 106). In this way the following equation was obtained:

$$\left(\frac{\partial \log q}{\partial \log\left(\frac{1}{[A]}\right)}\right) = -\frac{\partial \log q}{\partial p\,A} = 4 - \bar{n}, \text{ or}$$
$$\bar{n} = 4 + \frac{\partial \log q}{\partial p\,A} \quad . \qquad (58)$$

The method of finding the successive stability constants by means of Eqn. (58) has already been indicated briefly (p. 106).

The relative degree of association of hydrogen ions with metal-containing molecules in each of the phases can be determined by differentiating Eqn. (54) with respect to the hydrogen-ion concentration for constant concentrations of the metal ions and ligand:

$$\left(\frac{\partial \log q}{\partial \log [H]}\right)_{[M],[A]} = (\bar{E}\bar{H} - \bar{\varepsilon}\bar{h}). \qquad (59)$$

If MA_n molecules, which are not acido complexes, pass into the organic layer, the value of the derivative (59) is equal to zero for the case of mononuclear complexes, provided that no acido complexes are formed in aqueous solution, i.e. $\bar{h} = 0$. A possible value of this derivative indicates the extraction of acido complexes. If

$$\left(\frac{\partial \log q}{\partial \log [H]}\right)_{[M],[A]} < 0,$$

the species which had lost hydrogen ions pass into the organic solvent layer, and acido complexes are present in the aqueous solution, their distribution constants being extremely small or zero. In the extraction of internal complexes whose ligands are anions of weak acids HA, mononuclear complexes MA_n are generally formed in the aqueous phase, for which $\bar{E} = \bar{\varepsilon} = 1$ and $\bar{H} = \bar{h} = 0$. By using well known equations for the dissociation and distribution constants of HA in the given system and substituting the expression for [A] in Eqn. (54) it is possible to obtain

$$\log q = \Psi + (\bar{N} - \bar{n})(\log [HA]_{org} + pH - \log K_{diss\ HA}\ K_{part\ HA}). \qquad (60)$$

Thus from the slope of the $\log q = f(pH)$ curves for $[HA]_{org}$ = const. or the $\log q = f([HA]_{org})$ curves for pH = = const. the value of $\bar{N} = \bar{n}$ can be obtained. In the limiting case equations are obtained which had been deduced earlier by Kolthoff[10] and Irving[11]:

$$\log q = \Psi' + \bar{N}(\log [HA]_{org} + pH), \qquad (61)$$

where the constant Ψ' combines Ψ of Eqn. (60) with the remaining constants. As can be seen from Eqn. (61), the slope of the curve $\log q = f(pH)$ for $[HA]_{org}$ = const. is in the limiting case the value of $\bar{N}$, i.e. the mean number of ligands associated with a metal atom. In the case of mononuclear complexes $\bar{N}$ defines the composition of the extracted complex ($\bar{H} = \bar{h} = 0$). In certain systems this method was successful in establishing the composition of the extracted molecules[76,90,124,159]. Sometimes, owing to a number of causes (different ratios of stability and distribution constants[144]) the value of $\bar{N} - \bar{n}$ is obtained instead[24,41-43,91]. Particular cases of the determination of the composition of complex compounds in this way will be noted below. In certain cases it is necessary, in order to establish the composition of the complex species in each of the phases, to consider not one derivative but two in combination with supplementary information obtained by an independent method. If the acid HA is very strong (mineral acids such as HCl, HBr, etc.) and if the H^+ and A^- ions in the aqueous solution result solely from its dissociation, and provided that $[M] \ll [HA]_{total}$, then the concentrations can be equated: $[H] = [A] = [HA]_{total}$. Substituting these values in Eqn. (54) and differentiating yields the following equation for mononuclear complexes:

$$\left(\frac{\partial \log q}{\partial \log [HA]_{total}}\right)_{[M]} = \bar{E}(\bar{H} + \bar{N}) - \bar{\varepsilon}(\bar{h} + \bar{n}) = (\bar{H} - \bar{h}) + (\bar{N} - \bar{n}) \quad . \qquad (62)$$

The value of the derivative (62) in combination with such derivatives as

$$\left(\frac{\partial \log q}{\partial \log [H]}\right)_{[M],[A]} \quad \text{and} \quad \left(\frac{\partial \log q}{\partial \log [A]}\right)_{[M],[H]}$$

can give valuable information about the composition of the extracted complexes. For example, if the complex MA_3 passes into the organic phase, the values of the derivatives

$$\left(\frac{\partial \log q}{\partial \log [HA]_{total}}\right)_{[M]} \quad \text{and} \quad \left(\frac{\partial \log q}{\partial \log [A]}\right)_{[M],[H]}$$

are $(3 - \bar{n})$. At the same time if the organic phase contains an acido complex HMA_4 which dissociates strongly in aqueous solution into H^+ and MA_4^-, the values of these derivatives will no longer be $(3 - \bar{n})$, but $(5 - \bar{n})$ and $(4 - \bar{n})$ respectively, since for this case $\bar{H} = 1$, $\bar{h} = 0$, and $\bar{N} = 4$. If the acido complex is appreciably associated in the aqueous phase, or even if it dissociates appreciably in the organic phase, the position is greatly complicated and may require independent determinations of $\bar{n}$ or measurements of the electrical conductivity of the organic layer[144].

If it is established that a complex of type MA_n is extracted, it is easy to find its concentration in the aqueous phase when the extent of its formation, the total concentration of metal, and the concentration of free ligand [A] are known:

$$\frac{[MA_n]}{[M]_{total}} = \alpha_n = \frac{\kappa_n [A]^n}{\sum_0^n \kappa_n [A]^n}. \quad (63)$$

In such a case the partition coefficient of the metal is expressed by the equation

$$q = \frac{[MA_n]_{org}}{\sum [M]_{aq}} = \gamma_n \alpha_n = \frac{\gamma_n \cdot \kappa_n \cdot [A]^n}{\sum_0^n \kappa_n [A]^n}. \quad (64)$$

An analogous equation was obtained by Rydberg (see p. 104) and other investigators for the extraction of many internal complexes (e.g. for the distribution of thorium in two-phase systems in the presence of acetylacetone, oxine, cupferron, etc.). Eqn. (64) establishes a general relation between the partition coefficient of a metal, the distribution constant of the extracted mononuclear complex, and the stability constants of the various complexes in the aqueous phase.

If the acido complex HMA_{n+1} is involved in the distribution in addition to the complex MA_n, a new term will be introduced into the equation relating the partition coefficient to the parameters of the system:

$$q = \alpha_n \cdot \gamma_n + \alpha_{n+1} \cdot \gamma_{acido} \kappa'_{acido} [H], \quad (65)$$

where γ_{acido} is the distribution constant of HMA_{n+1}, and $\kappa'_{acido} = [HMA_{n+1}]/[H][MA_{n+1}]$ is its dissociation constant. The concentration of HMA_{+1} in the organic phase is obviously $\gamma_{acido}\kappa'_{acido}[H][MA_{n+1}]$. If several complexes are involved in the distribution, the equation can be given in the general form

$$q = \sum_0^n \alpha_i \gamma_i + \alpha_{n+1} \gamma_{acido} \kappa'_{acido} [H]. \quad (66)$$

If a sufficient number of experiments are carried out, Eqns. (64)–(66) can be used to calculate all the constants (distribution, stability, etc.) occurring in them. On the other hand, if the values of the stability and distribution constants are known, the proportion of each complex can be calculated as a function of the concentration of the free ligand [A]. More complicated equations are obtained if alkali-metal salts of acids of the type HMA_{n+1} take part in the distribution[144], but by appropriate modification of expressions similar to (65) and (66) formulae convenient for calculation can be obtained. In order to simplify equations of this type, it should be noted which of the complexes predominates in one of the phases, and whether its concentration in the other phase can be neglected.

A large number of complex compounds of metal ions with inorganic ligands have been investigated by the above procedures. Halide complexes have been studied in considerable detail, and among them perhaps the greatest attention has been devoted to the halide complexes of tervalent iron. The extraction of Fe(III) from chloride solutions by means of ether has been known for very many years[160-164], but the composition of the compounds formed in the aqueous phase, or distributed between the phases, let alone the stability of such compounds, remained unknown for a long time. It was noted that the partition coefficient depended on the components of the system[165,166], and subsequently many investigators, using various methods, studied the formation of complexes between Fe(III) and chloride ions, the composition of the extracted compound and of the complexes formed in the aqueous phase[145,157,158,167-176]. But when the results of all this work are collated, it is hardly possible to regard the problem of the composition or stability of these complexes as finally solved.

Other halide complexes which have been studied include chloride complexes of gallium[174,179-181], manganese[180], arsenic[182-184], thallium[152,174,185], and indium[150-152,186,187], bromide and iodide complexes of thallium[152], gallium[152], indium[150-152], and other elements[188]. In some cases the data obtained by the distribution method can be compared with the results of other methods of physicochemical analysis (e.g. chromatographic[189] or conductimetric[190]).

Irving and his collaborators[146-152] made a detailed study of the processes of complex formation in the systems In^{3+} – –hydrogen halide–organic solvent–aqueous phase. By using equations deduced previously[144], representing in a general form the extraction of complexes of this type, they were able to show that only the mononuclear complexes* $InBr^{2+}$, $InBr_2^+$, $InBr_3$, $HInBr_4$, and $InBr_4^-$ and free (hydrated) In^{3+} ions are formed at a concentration of $In^{3+} < 10^{-5}$ M in the aqueous phase in the presence of Br^- ions. At higher In^{3+} concentrations the formation of polynuclear complexes becomes possible. Irving and Rossotti found that, with trace concentrations of In^{3+} and the condition $1.0\ M \geqslant [Br^-] \leqslant 0.2\ M$ (pH $\geqslant 3$), every In^{3+} ion is combined on an average with 1.6 Br^- ions, but does not add on H^+ or OH^-. From solutions of low H^+ concentration ($\sim 10^{-3}$ M) $InBr_3$ and $MInBr_4$ (M = alkali metal) pass into the organic solvent layer. At higher acidities ($[H^+] > 0.1$ M) the acido complex $HInBr_4$ is preferentially extracted, and to a lesser extent $InBr_3$. Investigation of the extraction of In^{3+} from aqueous HBr solutions by isobutyl methyl ketone and diethyl ether, with $[In^{3+}] > 10^{-5}$, showed the presence in the aqueous phase of polymeric (associated) molecules containing In^{3+}. The value of the derivative $-1 \leqslant (\partial \log q/\partial \log[In])_{[HBr]} \leqslant 0$ [see Eqn.55)] indicates that mono- and dinuclear complexes exist in the aqueous phase and also that the monomeric form alone passes into the organic layer. Irving and Rossotti concluded from their results that the dimer In_2Br_6 ($In_2Br_7^-$ in the presence of KNO_3) predominates in the aqueous phase, and not hydroxylated dimers.

Recently Horrocks and Voigt[185] attempted to establish the composition of the complex compound extracted by ether from chloride solutions of $TlCl_3$. They showed that the partition coefficient of Tl(III) depends substantially on the ionic strength of the solution, the concentration of the ligand, and the hydrogen-ion concentration. With high ionic strength in the aqueous phase and a high Cl^- concentration in the ether layer, the complex of empirical formula $HTlCl_4$ is extracted, but not H_2TlCl_5. It was not possible, however, to explain the extraction process at low Cl^- and H^+ concentrations by

* Data on the stability of halide complexes of indium obtained by other methods (see for example Carleson and Irving[19]) also indicate that complexes of more complicated composition are absent.

this mechanism, and this forced Horrocks and Voigt to postulate that under these conditions either $TlCl_5$ is extracted or else $HTlCl_4$ dissociates in the organic phase.

The above equations are applicable only to ideal systems. In the case of "non-ideal" systems additional complications arise, and the distribution results can be interpreted either from a consideration of the phase diagrams[144] or by application of the Gibbs–Duhem equation, as was done by McKay et al.[192]. In the investigation of complex formation in solution by the distribution method non-ideal systems are encountered comparatively rarely, and they will therefore not be considered here.

Certain additional factors, which extend Irving's treatment were considered by Diamond in a series of papers on the extraction of complex compounds of sexivalent molybdenum. Nelidow and Diamond[193–196] measured the partition coefficient of Mo(VI) between various organic solvents (ketones, ethers, etc.) and aqueous HCl and HBr (occasionally with the addition of $HClO_4$ or trifluoroacetic acid) and studied its variation with the hydrogen-ion concentration and the concentration of the metal ions (between 10^{-9} and 10^{-2} M). From their results they attempted to deduce the nature of the complexes which were extracted and of those which remained in the aqueous phase. It was assumed that the mechanism of extraction is governed by four main factors: (1) association and polymerisation of metal-containing molecules in one or both phases (q should depend on $[M]_{aq}$); (2) ionisation of metal-containing species as an acid (q depends on the hydrogen-ion concentration and on the concentrations of any substances which dissociate with the formation of H^+); (3) complex formation with halide ions (q depends on the concentration of these and on the presence of components yielding halide ions on dissociation); and (4) solvation and hydration of complexes in each phase (q should consequently depend on the nature of the solvent). From a study of the variation of the partition coefficient with the metal-ion and hydrogen-ion concentrations, it appeared that the first two factors are of little significance, i.e. that the extracted molecules are monomers possessing no acidic properties. At the same time the effects of the third and fourth factors are quite distinct, and this led Diamond to conclude that the molecule which is extracted is MoO_2Cl_2 containing a variable number of added water and organic-solvent molecules (change in solvation with change in concentration of the acid is probably also significant).

Alimarin and Polyanskii[196] and also Zharovskii[197] studied an analogous system and explained the distribution curves they obtained by the formation of complex acids of the type $H[MoCl_5]$ and $H[MoO_2Cl_3]$.

Subsequently Diamond[194,195] made a further examination of the influence of the various parameters of the system (concentrations of halide ions, hydrogen ions, and foreign halide salts, acid strength, total concentration of metal) on the partition coefficients of halide complexes between aqueous solutions of hydrogen halides and various organic solvents. Apparently on the basis of considerations put forward in a short but interesting paper by Saldick[186], Diamond obtained general equations expressing the nature of the variation of q with change in the above parameters, taking into account the possible formation of cationic, neutral, anionic, and polymeric (associated) species containing ions of the metal under investigation. In contrast to the above method[144] of interpreting results for similar systems, the work of Diamond showed that the partition coefficient might be affected by the presence of substances containing an ion common to the ions of the complex compound formed, if such a substance predominates in one of the phases.

Diamond checked his equations for the distribution of molybdenum between aqueous solutions of HCl, HBr, and $HCl–HNO_3$ and $HBr–HClO_4$ mixtures, and various oxygen-containing organic solvents (diethyl, bis-2-chloroethyl, and dibutyl ethers, etc.). He showed that the change in partition coefficient with variation in the concentration of metal in the aqueous phase $[M]_{aq}$ might be caused by two main processes — polymerisation of metal-containing species in the aqueous phase and the influence of a common ion — which can be distinguished experimentally. If the decrease in the partition coefficient is due to polymerisation of metal-containing species in the aqueous phase, the slope of the $\log q = f(\log [M]_{aq})$ curve remains constant with different organic solvents and on introducing a second acid, which is more soluble in the organic solvent and dissociates more strongly in it than the hydrogen halide under investigation. If the change in the partition coefficient is due to the common ion effect the slope of the curve will depend on the nature of the solvent, and the partition coefficient of the metal in the given two-phase system will fall to a lower constant value on introducing the second acid (anions containing the metal then predominate in the organic phase, and halide ions in the aqueous phase). In this way it was shown that, at a concentration of the hydrogen halide below 6 M and a concentration of molybdenum ions below 0.1 M in the aqueous solution, polymeric forms can exist, but not monomeric cations to any appreciable extent, and the predominant species are apparently anions of acids which are stronger than HCl.

The distribution method is widely used in the investigation of nitrate complexes of actinides, lanthanides, and other elements. Such solvents as isobutyl methyl ketone[198], diisopropyl ether[199] and dibutyl ether[200] are comparatively seldom used for this purpose, but complex formation is very often studied by means of the distribution of the metal between an aqueous phase containing NO_3^- ions and a benzene solution of tri-n-butyl phosphate[201,202] (occasionally the benzene is replaced by paraffin oil [kerosene] and other solvents).

Fomin and Maiorova[203] investigated the distribution of HNO_3 between an aqueous phase and a solution of tri-n-butyl phosphate (TBP) in benzene. Povitskii and Solovkin and their collaborators[204,205] determined the equilibrium constant for complex formation between $HClO_4$ and TBP. Dyrssen[206] studied the dissociation, distribution, and dimerisation of dibutyl phosphate in an organic solvent.

The nitrates of many elements dissolve comparatively readily in TBP, forming complexes with the latter. The composition of such complexes can be established either by direct analysis of the compound formed (if this is possible, as in the case of $UO_2(NO_3)_2 \cdot 2TBP$ for example) or by studying the distribution of $M(NO_3)_p$ between H_2O and TBP. With constant ionic strength in the aqueous phase and a varying TBP concentration in the benzene (or other inert solvent) the partition coefficients of M^{p+} are determined for trace concentrations of the latter. Assuming that complexes $M(NO_3)_p \cdot nTBP$ exist in the organic layer and writing the equilibrium constant for the reaction $M^{p+} + pNO_3^- + nTBP \rightleftharpoons M(NO_3)_p \cdot nTBP$, it is easy to represent the partition coefficient,

$$q = \frac{[M(NO_3)_p \cdot n\ TBP]_{org}}{[M]_{aq}}, \qquad (67)$$

as a function of the TBP concentration. From the slope of the $q = f([TBP])$ curve we can find the number of TBP molecules associated with one molecule of the metal nitrate.

It is found that, depending on the experimental conditions, complexes are sometimes formed with different numbers of TBP molecules. In the case of $Th(NO_3)_4$ complexes are found with two [207-212] and four TBP molecules [213-215]. For other elements the following complexes are known:

$UO_2(NO_3)_2 \cdot 2$ TBP [207, 209, 213, 215-217], $Zr(NO_3)_4 \cdot 2$ TBP [209, 218, 219], $Zr(NO_3)_4$ TBP [220], $ZrCl_4 \cdot 2$ TBP [219, 221], $Y(NO_3)_3 \cdot 3$ TBP, $Ce(NO_3)_3 \cdot 3$ TBP, $Am(NO_3)_3 \cdot 3$ TBP [209, 222], $Ce(NO_3)_4 \cdot 2$ TBP, $Np(NO_3)_4 \cdot 2$ TBP, $NpO_2(NO_3)_2 \cdot 2$ TBP [209], $PuO_2(NO_3)_2 \cdot 2$ TBP $Pu(NO_3)_4 \cdot 2$ TBP [223].

The composition of the last complex has been confirmed by spectrophotometric measurements [224]. The extraction of compounds of uranium, thorium, ruthenium, lanthanum, and other elements by means of pure TBP and its solutions in various inert solvents has been studied by a number of Russian and foreign investigators [205, 225-231]. The distribution of nitrate complexes of Ce(IV) between an aqueous phase and a solution of tri-n-butyl phosphate was studied by Warf [232]. Subsequently Blaustein and Gryder [199] detected polymeric molecules in aqueous solutions of cerium nitrate. They showed also that the complex $H_2Ce(NO_3)_6$ passed into the organic solvent layer*. Analogous results were obtained also by Wylie [234]. The distribution method has been used to study complexes of protactinium with alkyl hydrogen phosphates [235, 236], mixed complexes of thorium with sulphate and nitrate ions [237], and several complexes of astatine [238] and uranium [239].

A number of investigations have been made into the composition of thiocyanate complexes of metals. As early as 1931 Schlesinger and Van Valkenburgh [240] attempted to establish spectrophotometrically the composition of the thiocyanate complex of Fe(III) extracted by ether. They concluded that the dimer $Fe[Fe(SCN)_6]$ exists in the ether. MacDonald, Mitchell, et al. [241, 242], by making a detailed study of all the factors influencing the extraction of iron thiocyanate, proved subsequently that this conclusion was erroneous. They showed that the ether layer contains the complex $Fe(SCN)_3$, while the aqueous phase contains a series of complexes $Fe(SCN)_x^{(3-x)+}$, where $x = 1-6$. The extraction of thiocyanate complexes of Fe(III) and of a number of other elements by means of n-butyl phosphate, tri-n-butyl phosphate, and diethyl ether was also studied by Freiser [243, 244] and Bock [245].

Other types of complex compounds which have been studied include complexes of nickel with organic acids and amines [246-249], compounds of calcium with hydrazine [250], phosphate complexes of uranium [251], and certain perrhenates [252]. Work has been done on the reactions of iodine in aqueous solutions and on other special problems [253-258]. In certain cases results obtained by the distribution method are in very good agreement with data obtained by other methods (e.g. potentiometric [259] or chromatographic [249]).

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This account shows that appropriate mathematical procedures for treating the experimental results to obtain information on the composition and physicochemical characteristics of complex compounds are available for every system. A complete study of the process of complex formation in systems containing internal complexes falls into a series of stages, none of which can in general be excluded: (1) determination of the dissociation constants of an organic reagent HA for a given constant ionic strength and temperature; (2) study of the distribution of the reagent between the aqueous phase and several (at least two) organic solvents over a fairly wide range of HA concentrations in the organic layer; (3) ascertaining the range of concentration of metal ions in the aqueous phase within which formation of polynuclear complexes and hydrolysis products may be neglected; (4) an examination of the possible formation of complexes containing molecules of the organic solvent; (5) establishment of the composition of the complexes formed in the aqueous phase; (6) plotting of the distribution curve for a reasonable selection of the above factors and its mathematical treatment by one or more methods of calculation [48-52, 260] (sometimes both arithmetical and graphical* methods can be employed in the treatment of experimental results). The examination of various special systems (complex formation with organic or inorganic ligands, employment of polar or non-polar organic solvents, etc.) may sometimes require appropriate modification of the above equations to allow for the peculiarities of the particular system.

The mathematical procedures employed in the study of complex formation by the distribution method are now quite well developed. Almost all the types of complexes that can be formed in aqueous solutions have been discussed theoretically. Many such complexes have been studied experimentally, at least in solutions of low and constant ionic strength.

The theoretical principles discussed here and the brief account of the vast range of systems investigated by the distribution method show it to be reliable, rapid, and comparatively simple. The determination of the stability constants of complex compounds, and also of such important properties as the partition coefficient of the metal and the distribution constant of complex molecules in various two-phase systems opens up wide opportunities for the solution of both theoretical and practical problems in analytical and other fields of chemistry.

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* These results may be compared with the data of Newton and Arcand obtained with sulphate complexes of cerium [233].

* For graphical treatment of the results of investigations of complex formation see, for example, Rossotti et al. [261-264].

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POLYMERIC CHELATE COMPOUNDS

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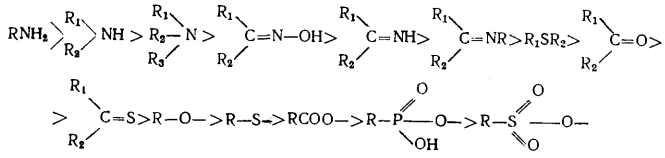
The development of modern polymer technology poses the complex problem of producing polymers possessing, in addition to high thermal stability, a high electrical conductivity, magnetic permeability, electron-exchange capacity, and many other special properties.

The solution of these problems requires the development of new routes to the synthesis of polymeric materials which possess the easy workability, chemical stability, and specific physico-mechanical properties characteristic of many organic and organometallic polymers, and the thermal stability, electrical conductivity, magnetic permeability, etc., of metals.

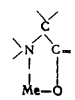
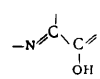
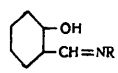
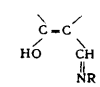
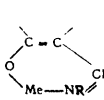
At present there are prospects of methods which might lead to new types of polymers, having a wide range of properties. Among these new methods is the synthesis of polymeric chelate complexes.

It is known[1] that chelate complexes are usually insoluble in water and show high stability towards the action of acids, alkalis, and reagents which react with the free metal ion. Many chelate complexes are very stable at comparatively high temperatures (400° or more). Compounds which form chelate complexes contain strongly polarised electron-donor and electron-accepting groups; in most cases these groups are present in a conjugated chain, which allows the unshared electrons to move towards the more electronegative atom or group.

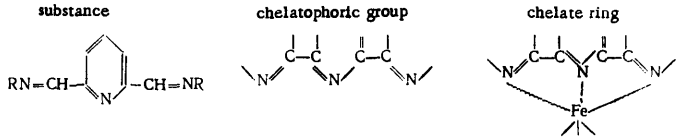
Groups which can form chelate rings are conveniently called chelatophores*. The electron-donor groups which form chelatophores may be arranged in the following series:



These groups when present in a molecule form chelate rings in the presence of an electrophilic ion or atom, the stability of the resulting rings being considerably increased if the above groups are present in a conjugated chain. This is illustrated by the following examples.

Substance	Chelatophoric group	Chelate ring
NH_2CH_2COOH		
		
		

In certain cases the complex-forming group contains more than two atoms capable of forming chelate rings with metal atoms; such chelatophores are called "tridentate" (with three such atoms), "tetradentate" (with four atoms capable of forming rings with a metal), and so on. The following is an example of a tridentate chelatophore:

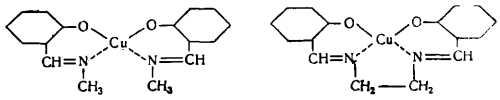


* Author's definition (Ed. of Translation).

The chemical and thermal stability of the chelate ring depends on a number of factors, including the structure and chemical nature of the chelatophore, the strain in the cyclic structures, the number of rings joined to the given ion, and the electronic structure of the complex-forming ion. Depending on the structure of the chelatophore, chelates with 4, 5, 6, 7, 8 or more atoms in the ring are formed. With a planar disposition of atoms, the five- and six-membered rings are the most stable. They are formed by the reaction of metal ions with ethylenediamine, diethylene triamine, *o*-hydroxyacids (e.g. salicylic acid and its derivatives), β-diketones (e.g. acetylacetone and benzoylacetone), 8-hydroxyquinoline, 1-hydroxyanthraquinone, etc.

According to Bayer's theory, the five-membered ring has the least strain; however, when the ring is made up of alternating single and double bonds, the six-membered ring is the most stable, since complete conjugation is then possible, with the greatest gain of energy.

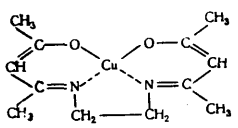
These considerations also apply in the chemistry of chelate compounds. Pfeiffer[2] has shown that five-membered chelate rings are more stable than six-membered when there are no conjugated double bonds in the resulting chelate. The more rings formed when the chelatophore reacts with the metal ion or atom, the lower will be the internal energy on the formation of the stable cyclic structures. This has been confirmed by Calvin and Bailes[3], who showed that chelate compounds in which the metal atom is a member of several rings are more stable chemically and thermally than analogous compounds with fewer rings. Thus the half-wave potential of a complex with three chelate rings is considerably lower than that of an analogous complex with two such rings; for instance, the Schiff's bases obtained from salicylaldehyde and methylamine and ethylenediamine have half-wave potentials of ±0.02 and -0.75 respectively:



The Table gives the logarithms of the stability constants for various chelates of Zn and Ca.

Chelates of Zn with:	log k (Σ log k_n)	Chelate of Ca with:	log k (Σ log k_n)
Ethylenediamine (2) rings	11.1	Methylaminodiocetic acid (4 rings)	7.5
Triethylenetetramine (3 rings)	14.6		
Aminodiacetic acid (4 rings)	13.5	Ethylenediamine tetraacetic acid (5 rings)	10.6
Ethylenediamine tetraacetic acid (5 rings)	16.6		

The presence of several rings in a chelate also makes these compounds more stable towards heat. Thus, for instance, copper ethylenediamine-bis-acetylacetonate



is hardly decomposed at red heat[5], and copper phthalocyanine sublimes in a vacuum at 570° without decomposition[6].

The stability of the complex depends on the type of bond between the metal ion and the chelatophore donor groups[7] and on the electronic structure of the ion.

There is a definite relationship between the chemical stability of the complex and the nature of the metal ion. Mellor and Maley[8] studied the stability of salicylaldehyde complexes in 1:1 water–dioxan. The metals lie in the series Pd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+}, Mn^{2+}, Mg^{2+} in order of decreasing stability of the complex. Almost the same order was found by Pfeiffer[9] for the complexes of Cu, Ni, Fe, Zn, and Mg with ethylenediamine and 8-hydroxyquinoline, and by Van Uitert and coworkers[10] for the complexes of Ag^{2+}, Cu^{2+}, Be^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Pd^{2+}, Mn^{2+}, Cd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} with β-diketones.

The chemical stability of the chelates decreases with increasing basicity of the metal; the most weakly basic metals (Pd, Cu) form the most stable complexes. Thus the chemical stability of the chelates decreases with increasing ionic character of the bond between the metal and the atoms of the chelatophoric group.

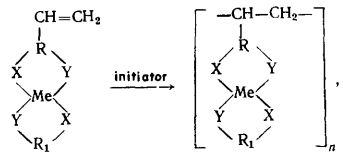
In most cases the chelate complexes are distinguished by a comparatively high chemical stability. For example, the copper salt of ethylenediamine tetraacetic acid is unchanged on boiling with alkali[11]. The stability of the chelates of the alkaline-earth metals with ethylenediamine tetraacetic acid is so great that the metals are not precipitated as sulphates, oxalates, phosphates, carbonates, etc. The glycinate and alaninate of Co^{3+} dissolve in concentrated sulphuric acid without any substantial chemical change. Beryllium salicylates are only slightly decomposed by alkalis[12].

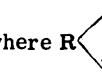
It would be expected, from these distinctive properties of the chelate compounds, that polymeric chelates would possess many interesting properties.

From the chemistry of synthetic polymers and the theory of complex compounds, the following four methods for the synthesis of polymeric chelates (polychelates) may be considered.

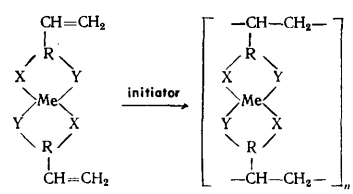
1. The polymerisation of monomers containing a metal atom joined in a chelate ring:

   (a) the formation of linear or low-branched macromolecules:



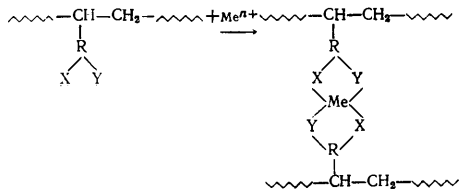
   where  is the chelatophore, Me is the metal atom, and R_1 is an aromatic, alicyclic, or acyclic radical;

   (b) the formation of three-dimensional or highly branched macromolecular structures:

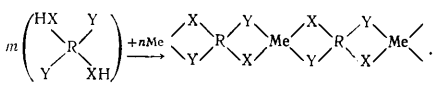


2. The synthesis of polymers by the polycondensation of substances containing chemically stable chelate rings; this can be achieved by the reaction of low-molecular substances containing chelate rings and at least two reactive groups (carboxyl, hydroxy, amino, ester, alkoxy, etc.).

3. The synthesis of polymers by the reaction of carbo- or hetero-chain polymers containing chelatophoric groups, with metal ions or atoms; soluble (linear, branched) and insoluble (cross-linked) polymers can be produced:



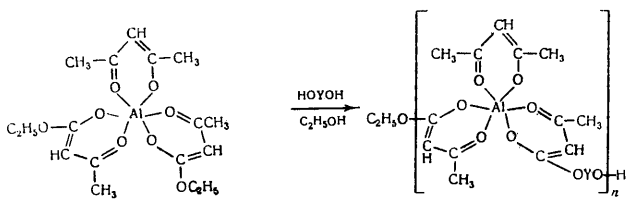
4. The synthesis of polymers from complex-forming low-molecular substances and metal ions or atoms. This method, as distinct from the preceding methods, can produce polymers in which the macromolecules are built up with covalent and coordinate bonds; such a reaction should be called polycoordination. The principle of the method is shown in the diagram[13]:



Depending on the structure of the original chelatophore and the nature of the metal ion, the polycoordination reaction can produce polymers of linear (ribbon), planar, or three-dimensional structure.

It may be expected that by combining various monomers containing chelatophoric groups, copolymeric-polycondensation and, in particular, polychelate compounds with a wide range of physical and physicochemical properties could be prepared. The use of the polycondensation reaction for the synthesis of block and graft copolymers is also of great interest.

At present, the synthesis of polymeric chelate compounds is in the initial stage of development. There are as yet no published references to the preparation of such polymers by type 1 reactions. Polymers containing aluminium chelates have been prepared by a reaction of the second type. Patterson and coworkers[14] have prepared polymeric chelates of the following structure by the condensation of diols with monomeric aluminium chelates containing groups capable of further reaction:



where HOYOH is a diol.

The resulting polymers are solid transparent coloured substances, soluble in benzene. They can be drawn from a melt into long brittle fibres, but have low thermal stability; they all decompose above 200°.

TABLE 1. Properties of the polychelates obtained by the reaction of aluminium acetylacetonate bis-(ethyl acetoacetate) with diols.

Diol	Softening temp. of the polymer, °C	Molecular wt. of the polymer
Ethylene glycol	105—120	1370* 2020**
Diethylene glycol	105—110	980**
Triethylene glycol	75—130	1100**
Butane-1,3-diol	100—110	2620*
Butane-1,4-diol	95—150	940**
Pentane-1,5-diol	80—100	1570**

* Molecular weight determined by acetylation of the end groups.

** Cryoscopic method in benzene.

Attempts to produce polymers of higher molecular weight by heating these polymers in a vacuum at 200°–250° failed, since under these conditions acetylacetone is split off and no cross-etherification takes place.

Polymeric chelates have also been prepared by the condensation of diisopropylaluminium monoacetylacetonate with a number of compounds containing two chelatophoric groups. These compounds are similar to those described above; they also do not have a high thermal stability, decomposing with the liberation of acetylacetone above 200°. Some of these polymers are insoluble and do not melt, which is explained by the great rigidity of the main polymer chain:

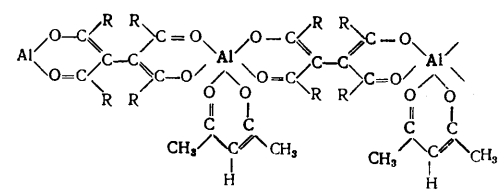


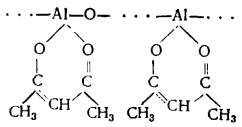
TABLE 2. Properties of the polymers obtained by the condensation of diisopropylaluminium monoacetylacetonate with various compounds.

Compound	Form of the polymer	Softening temp. of the polymer, °C	Molecular wt. of the polymer
Ethylene-bis-(acetoacetate)	solid yellow transparent	130—150	770
Diethylene-glycol-bis-(acetoacetate)	»	80—150	930
Tetramethylene-bis-(acetoacetate)	pale-yellow, transparent	75—95	1160
Pentamethylene-bis-(acetoacetate)	»	40—45	450
2,4-Diacetylresorcinol	rust-brown *	>360	—
2,2'-Bis-(ethyl-acetoacetate)	»	>360	1860
1,1,2,2-Tetraacetylethane	granular, white	>360	—
1,1,2,2-Tetrabenzoylethane	mainly original substance separated		
α,α-Methylene-bis-(ethylacetoacetate)	brittle brown	110—130	1275
1,1,3,3-Tetraacetylpropane	dark red, transparent	90—150	1070
1,1,3,3-Tetrabenzoylpropane	brittle, amber colour	130—145	920

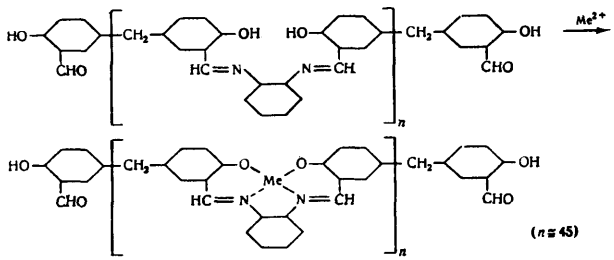
* Insoluble in organic solvents.

All the polymers apart from the one marked with an asterisk (Table 2) are soluble in benzene; molecular weights were determined cryoscopically.

The high-temperature hydrolysis of dialkoxyaluminium acetylacetonate[15] is the same type of reaction. It is known that this interesting reaction takes place with the loss of two molecules of alcohol for each molecule of complex, forming a polymeric product, probably having the structure

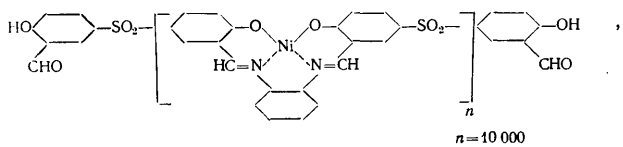


Marvel and Tarkoy[16] have recently described the conversion of carbo- or hetero-chain polymers containing chelatophoric groups into a polymeric chelate compound (reaction 3). The starting material was the Schiff's base obtained from methylene-(bis-salicylaldehyde) and *o*-phenylenediamine; the reaction of this polymer with acetates of Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Fe^{2+} in a mixture of tetrahydrofuran with water or acetic acid produced a polymer with chelate linkages.



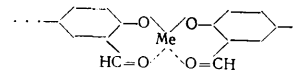
These polymers are insoluble and vary in colour from orange to dark brown, depending on the metal. The thermal stability of the polymers also depends on the metal, and increases in the series: Cu, Co, Zn, Ni, Fe, Cd. On heating at 250° for 3 h these polymeric complexes lost 11–26% of their weight, partly because of the loss of water of crystallisation (1–2 moles of H_2O per atom of metal).

Increased thermal stability as compared with the polymers prepared by Marvel and Tarkoy[16] is found if the methylene groups are replaced by sulphone groups $-SO_2-$;[17] thus the polymers based on the polymeric Schiff's base from bis-(salicylaldehyde-5,5-sulphone) and *o*-phenylenediamine:



lose only 0.3% of their original weight on heating at 250° for 3 h.

It is interesting that the thermal stability of the compounds mentioned above is almost independent of whether it is measured in air or in nitrogen, indicating that these compounds are relatively stable to oxidative destruction. It may be assumed that the polymeric chelates of the above structure can form their own block polymers because of the existence of the terminal hydroxy and aldehyde groups; the metal atom joins separate macromolecules with the formation of longer chains:



The formation of insoluble chelates of Cu, Zn, Fe, Sn, and other metals with the linear polymers obtained by the reaction of salicylaldehyde with polyamines has been reported[18].

Among the polymers with chelate bonds are the salts of polymethacrylic and polyacrylic acids with Cu^{2+} [19-21] and other metals. Various methods of studying these polymeric complexes have shown that the copper atom is linked to two or four carboxyl groups[19,20,22-24]. These complexes are considerably more stable than complexes of the monomeric analogue, glutaric acid[24], probably because of the influence of the polyelectrolyte field or the presence of vicinal structures in the polyacrylate chains.

It is interesting that polymers containing isolated carboxyl groups show only a slight adsorption of Cu^{2+}, La^{3+}, Mg^{2+}, and K^+,[25] as compared with the adsorption of Cu^{2+} by polymethacrylic acid.

Polyacrylic acid forms complexes with Mg^{2+}, Ca^{2+}, Co^{2+}, Mn^{2+}, and Zn^{2+}.[26] The ions of Ca, Sr, and Ba cause gelatinisation of solutions of polyacrylic acid, the activity of the ions falling in the series: Ba, Sr, Ca.[27] The ions Ni^{2+}, Co^{2+}, and Zn^{2+} have a low tendency to complex formation with polyacrylic acid[20].

The ability of acrylic acid polymers and copolymers to form stable non-melting and insoluble compounds with ions of di- and polyvalent metals had already been found in 1946 by Berlin[28], who suggested this reaction for the preparation of thermally stable plastics.

Morawetz and coworkers[29] studied the chelates of Mg, Ca, Sr, and Ba with hydrolysed copolymers of maleic anhydride and styrene or vinyl ethyl ether.

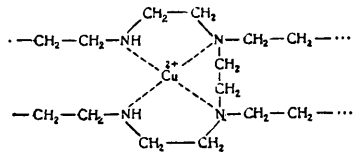
The polymeric keto-ester obtained by the hydrolysis of poly(ethyl-3-ethoxy-2,4-pentadienoate) complexes with Cu^{2+} is a pale green solid which does not melt up to 205° (the original polymer has m.p. 90°–125°) and which is insoluble in solvents which dissolve the original polymer[30].

The preparation and properties of polyvinyl acetoacetate[31] and the polychelates from polyvinylacetonylketone with salts of Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, UO_2^{2+}, Pr^{3+}, and Nd^{3+},[32] have been described.

After treatment with alkali, the copolymer prepared from methacrylylacetone (2-methylhex-1-ene-3,5-dione) and 10% ethylene glycol dimethacrylate in the presence of 1% azodiisobutyronitrile adsorbs Fe^{2+} and UO_2^{2+} ions at definite pH values below 7. The ability to extract Fe^{2+} and UO_2^{2+} ions is also possessed by the copolymers prepared from methacrylylacetone and methacrylic acid in the ratio 1:1 or 1:2 and 10% ethylene glycol dimethacrylate in the presence of azodiisobutyronitrile and water. These resins easily exchange iron and uranyl ions and have been suggested for use as ion-exchange resins[33].

Chelate compounds are also formed by the reaction of monovalent copper ions with polyacrylonitrile and its copolymers[34-37], the copper ions forming complexes of coordination number 4 with the cyano groups of polyacrylonitrile.

The phenomenon of complex formation is widely used for the selective extraction of metals with ion-exchange resins. Polyethylene-imine cross-linked with dibromoethane forms stable complexes with divalent copper and less stable complexes with Co^{2+}, Ni^{2+}, and Zn^{2+}:[38,39]



For the extraction of metals, Gregor and coworkers[40] synthesised a number of resins from *m*-phenylenediglycine and formaldehyde, anthranilic acid, resorcinol, and formaldehyde, and *o*-aminophenol and formaldehyde[40,41]. These resins form complexes with Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} at pH 5, the resin from anthranilic acid extracting the metals to a lesser degree, probably because of the presence of a very fine lattice.

Parrish[41] prepared a resin from resorcinol, pyrogallol, and formaldehyde which forms complexes with Ba^{2+}, Ca^{2+}, and Sr^{2+}. He also prepared a resin by diazotising the *o*-aminophenol resin and coupling with 2-naphthol; this complexes with Mg^{2+} and Cu^{2+} at pH 3. An *o*-aminophenol--formaldehyde resin, obtained by reducing the *o*-nitrophenol-formaldehyde resin, complexes easily with Cu^{2+} in the presence of Ca^{2+} at pH 5.5.

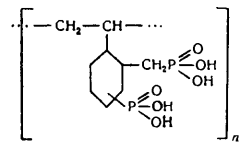
Diazotisation of an amino resin and coupling with 8-hydroxyquinoline enabled Parrish[42] to synthesise a product which adsorbs the ions of various metals at different pH values; at pH 2–3 it adsorbs Cu^{2+}, Ni^{2+}, and Co^{2+}, and at pH 1.5, 2.0, 2.8, 4.0, and 4.8 it adsorbs Zn^{2+}, Mn^{2+}, Al^{3+}, Mg^{2+}, and Ca^{2+} respectively.

The coupling of diazotised polyaminostyrene with *o*-hydroxyphenylarsonic, salicyclic, or kojic acids, enables ion-exchange resins having an affinity for copper ions to be obtained. Similar resins are prepared by condensing resorcinol with formaldehyde and certain acids[43]. Resins which selectively extract heavy metal ions are obtained by condensing a mixture of resorcinol and anthranilic acid (or 8-hydroxyquinoline) with formaldehyde[44].

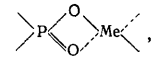
The polythiols obtained by hydrolysing the reaction product of thiourea with chloromethylated polystyrene selectively adsorb Hg^{2+} in the presence of Mg^{2+} at pH 7.[42]

The introduction of complex-forming substances enabled Klyachko[45] to synthesise resins which selectively extract metal ions. Thus by condensing phenol sulphonic acid with formaldehyde and ethylenediamine tetraacetic acid a resin is obtained which selectively extracts Ca^{2+}. The introduction of dimethylglyoxime into a sulpho-resorcinol cation--exchange resin gives a resin which complexes with Ni^{2+}. The addition of 1,8-dihydroxynaphthalene-3,6-disulphonic acid in the preparation of sulpho-phenol cation-exchange resin gives a resin which forms chelates with titanium, gold, vanadium, and other metal ions.

The work of Kennedy and coworkers[46–48] on the phosphorylation of chloromethylated styrene cross-linked with divinylbenzene is of considerable interest; the resulting polymers contain the group:



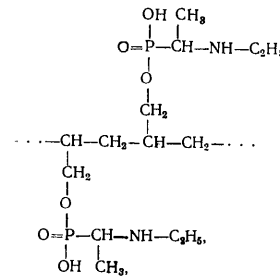
and form four-membered chelate rings with metal ions:



the activity of the resin towards various ions decreasing in the series:

$$Th^{4+} \text{ and } U^{4+} > UO_2^{2+} \cong Fe^{3+} > \text{rare earths}^{3+} > H^+ > Cu^{2+}, Co^{2+}, \text{ and } Ba^{2+} > Na^+.$$

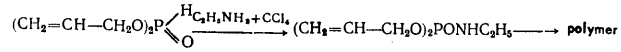
Treating polymeric diallyl phosphate with acetaldehyde-ethylene-imine with subsequent hydrolysis gives polymers containing the chelatophoric groups



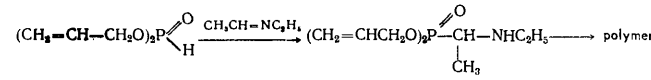
and these form stable complexes with ions of metals of variable valency[46–48].

Kennedy, Lane, and Robinson[47] have prepared a number of phosphorylated polymers by the partial hydrolysis of polymeric allyl phosphates, by the reaction of polyvinyl chloride or channel black with PCl_3 in the presence of $AlCl_3$, and by treating phenol-formaldehyde resin with tetraethylpyrophosphate in alkaline medium.

Kennedy and Ficken[48] synthesised polymeric phosphonamides and α-aminophosphonates by the reactions:

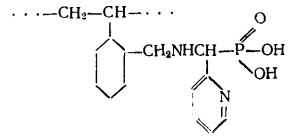


Poly-α-aminophosphonates were prepared from polymeric diallyl hydrogen phosphonate by reaction with Schiff's bases:



A series of polymers was prepared in this way; complex-forming groups are formed on partial hydrolysis.

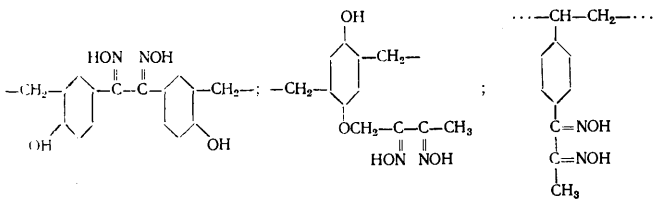
Polyaminomethylstyrene gives with pyridine-2-aldehyde a polymer which reacts with diethyl hydrogen phosphonate; hydrolysis of the resulting product gives a polymer which is capable of forming complexes:



Resins which form polychelates are obtained by condensing with formaldehyde the reaction products of salicyl or resorcyl aldehyde with dialkyl phosphites or phosphoric acid[49].

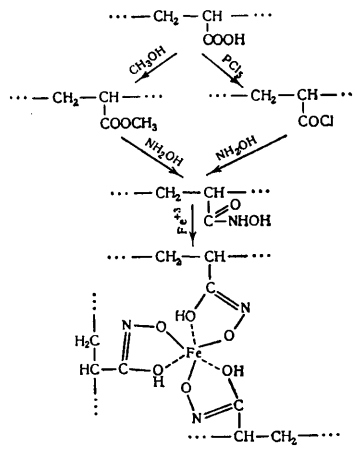
Phosphorylated cellulose is used for the chromatographic separation of Cu, Fe, and Ni ions and the partial separation of Au, Pd, Pt, and Rh[50]. Other phosphorylated resins also form complexes with metal ions[51,52]

Štamberg, Seidel, and Rahm[53] have synthesised three polymers which selectively extract Ni^{2+}; they have the structures

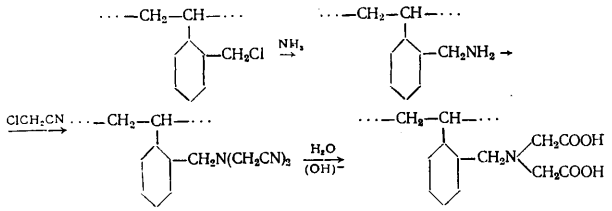


Polymers which complex with Fe^{3+} and selectively extract these ions from solution have been prepared by Cornaz and Deuel[54] and Hale[55] from polymeric carboxylic acids and by Kern and Schulz[56] from polyesters.

The formation of polyacrylic-acid derivatives containing chelatophoric groups and the structure of the chelates obtained from them may be represented as follows:

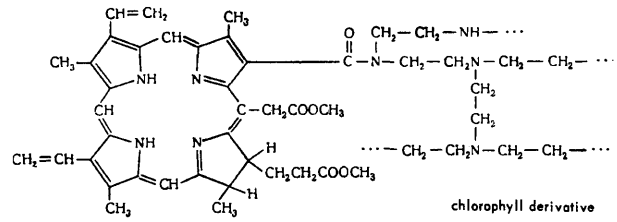


Chloromethylated polystyrene can be converted into a polymer which complexes with the alkaline-earth metals and serves for their extraction[41]:



Similar resins which complex with Cu^{2+} have been prepared from chloromethylated polymers by reaction with various aminoacids, for example methylaminodiacetic acid, dimethylaminoacetic acid, methylethanolaminoacetic acid, etc.[57].

Polymers containing chlorophyll and haemin residues are interesting examples of polymeric materials which form chelates; such substances form stable complexes with Fe^{2+} [58,59].

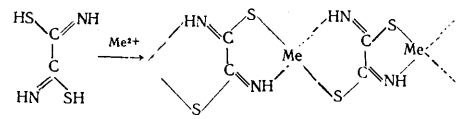


The copolymers of 2-vinyl- and 2,4-divinylhaemins with styrene[60] are of great interest in this respect.

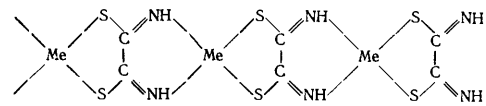
It is seen that by suitable reactions it is possible to synthesise various polymers which are capable of forming complexes with metal ions, and so obtain a large number of various cross-linked polychelates which are of considerable practical interest as ion adsorbents.

One of the most interesting, but little developed, methods of synthesis of polymeric chelates is the polycoordination reaction of low-molecular compounds containing chelatophores. Inorganic and organic polymers can be prepared by this reaction.

Jensen[61] describes the polymeric chelates of dithiooxamide (rubeanic acid) with Ni^{2+} and Cu^{2+}:



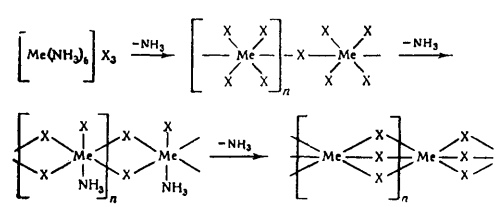
Study of their infra-red spectra shows the presence of the NH bond[62]. From X-ray spectrographic studies of crystalline rubeanic acid, this polymer is given the *trans*-structure; however, Xavier and Ray[63] suggest that the polymer may exist in the *cis*-form:



The polymeric compounds of rubeanic acid with copper are insoluble in water; the Ni, Co, and Pd polychelates are soluble in pyridine.

It has been found that films coated with rubeanic-acid polychelates pass light in one direction only, apparently because of the parallel orientation of the polymer chains[64].

In 1956 Schmitz-Dumont[65] reported the preparation of the polymeric complexes

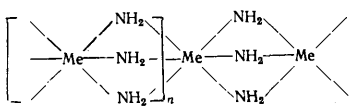


where Me = Co^{3+} or Cr^{3+}, and X = NO_3.

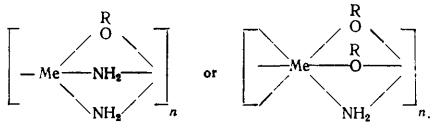
Replacing the residue X by the NH_2 group gives the metal amides

$$[Me(NH_3)_6](NO_3)_3 \xrightarrow{KNH_2} [Me(NH_3)_6](NH_2)_3 ,$$

which, on losing NH_3, are converted into polymeric complexes



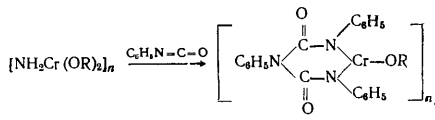
By splitting out alcohol and NH_3 from Co(III) or Cr(III) hexammine alcoholate, polymeric complexes are obtained of the type



The synthesis of inorganic polymeric complexes is an example of polycoordination in which other products are also liberated, i.e. it is analogous to polycondensation. All the complex polymers reviewed above are amphoteric, reacting with both NH_4X and KNH_2 in liquid NH_3.

The polymeric metal amides react with diphenylketene and phenyl isocyanate[65]:

$$[NH_2Cr(OCH_2C_6H_5)_2]_n + n(C_6H_5)_2C{=}C{=}O \rightarrow [(C_6H_5)_2CHCONHCr(OCH_2C_6H_5)_2]_n$$



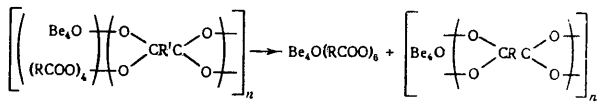
The reaction of organic phosphorus compounds with MoO_3 and 90% H_2O_2 gives polymeric complexes which are stable up to 150°–160°,[66] the structure of which cannot be considered as definitely established.

In 1940 Holland[67] reported the formation of polymeric complexes of chromium with succinic, fumaric, glutaric, suberic, adipic, azelaic, and phthalic acids, and in 1950 Shuttleworth[68] confirmed this.

The basic beryllium carboxylates $Be_4O(RCOO)_6$, which are covalent compounds, possess a fairly high thermal stability, and can be sublimed without decomposition at atmospheric pressure above 300°–350°. In 1907 Tanator and Kurovskii[69] prepared basic beryllium succinate, but it was not identified as a polymer, although it is a solid infusible glass, and is probably of three-dimensional structure.

Marvel and Martin[70] (1958) studied the possibility of, and the conditions for, the replacement of the monocarboxylic acid residues in the basic beryllium carboxylates by dibasic acid residues with the object of obtaining thermostable polymeric materials. Equimolecular quantities of beryllium acetate, propionate, or benzoate and adipic, β-ethyladipic, sebacic, isophthalic, or terephthalic acid dichlorides were heated in toluene or other solvent for 16–20 h, and the polymer precipitated with petroleum ether. All the polymers are powders with a degree of polymerisation of 4–6.

The polymers containing only aliphatic acids possess limited elasticity on plasticising with a small amount of solvent, and can be drawn into short filaments. They are not decomposed above 400°, but the linear polymer disproportionates to form three-dimensional structures; this takes place even at room temperature:

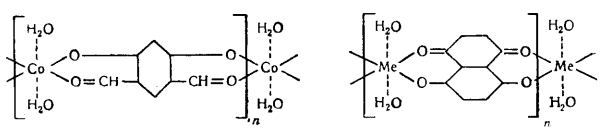


The polymers containing aromatic acids are somewhat more stable to disproportionation, but at 340° they also disproportionate quite readily.

Insoluble three-dimensional polymers are obtained when the polycoordination is carried out by fusing basic beryllium propionate with sebacic, adipic, and terephthalic acids.

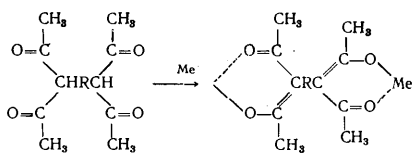
Polymeric beryllium carboxylates have also been prepared by polymerising beryllium methacrylate pentapropionate and beryllium hexamethacrylate in the presence of benzoyl peroxide, but the polymer derived from the former was only very slightly soluble. Both substances are white powders which decompose vigorously at 200°. The low thermal stability of such polymers is probably due to the presence of the main carbon chain; however, poly-beryllium methacrylate pentapropionate is more stable to heat than many polymethacrylic and polyacrylic esters.

Polymeric complexes of Co^{2+} with 4-hydroxy-5-formylsalicyl aldehyde[71], of Co^{2+} and Be^{2+} with naphthazarin[71,72], and of Cu^{2+}, Fe^{2+}, Hg^{2+}, and Ag^{2+} with 2,5-dihydroxybenzoquinone[73] have been described:



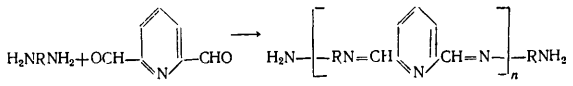
where Me = Co^{2+} or Be^{2+}.

In 1954 Wilkins and Wittbecker[74] proposed a new method for the production of thermostable polymers suitable for the preparation of fibres, films, and coatings, by the reaction of tetraketones with salts of the divalent metals Be, Cu, Ni, Zn, Co, Fe, Pb, Mn, Ca, Ba, Sr, and Cd. The polycoordination reaction can be effected by heating a mixture of a tetraketone and beryllium acetylacetonate at 200°, the acetylacetone liberated being distilled off. Suggested tetraketones are terephthaloyl bis-acetone, *p*-bis-(2,2-diacetylethyl)benzene and bis-(*p*-acetoacetyl)phenyl ether:

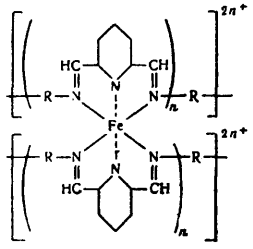


The polymeric chelate compound from terephthaloyl bis-acetone has a melting point above 285° and is insoluble in boiling benzene and dimethylformamide. The polymeric complex from bis-(*p*-acetoacetyl)phenyl ether is insoluble in a mixture of methanol and chloroform.

Lions and Martin[75] obtained infusible polymers by the polycondensation of pyridine-2,6-dialdehyde with ethylenediamine, hexamethylenediamine, and benzidine:



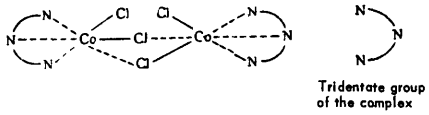
The polymer derived from benzidine possesses a very slight tendency to coordinate with Fe^{2+}, but forms polychelates with $CuCl_2$. The polymers from ethylenediamine and hexamethylenediamine react easily with Fe^{2+} on boiling an aqueous suspension of the polymer with excess $FeSO_4$, forming dark red products which are insoluble in the usual solvents and are not decomposed or melted up to 300°; they have the structure:



i.e., each metal atom combines with two tridentate residues of the polymer. This polymer has very unusual magnetic properties — it is ferromagnetic with molar magnetic susceptibility $155\,000 \times 10^{-6}$ cgs units.

In the preparation of the polymeric chelate by reacting pyridine-2,6-dialdehyde with ethylenediamine in the presence of $FeSO_4$ in aqueous alcoholic solution, a soluble polymer is formed, in which two iron atoms are combined with seven tridentate residues. The perchlorate of this polymer has diamagnetic properties. The authors find it difficult to explain such unusual magnetic properties in these polychelates.

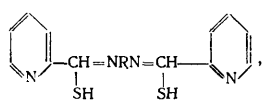
The reaction of the polymeric Schiff's base with Co^{2+} salts ($CoCl_2$) produces a paramagnetic polymer in which each tridentate group combines with one cobalt atom (magnetic movement, 3.7 Bohr magnetons). This polymer is given the structure



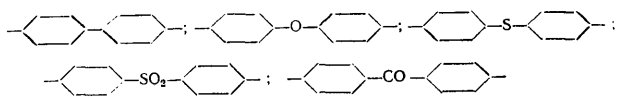
Tridentate group of the complex

the existence of chlorine bridges being assumed.

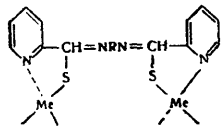
In 1958 the synthesis of polymers of chelates based on bis-α-thiopicolylamides was reported[13].



where R =



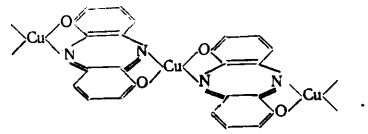
They are prepared by mixing stoichiometric quantities of a solution of bis-α-thiopicolylamides in dimethylformamide and a methanolic solution of metal (Cu, Ni, Zn) acetates, the polymer precipitating almost immediately. To complete the reaction the solution is heated for half an hour. The polymeric chelates are insoluble in organic solvents and do not melt below 300°. Analysis and their infra-red spectra confirm the structure



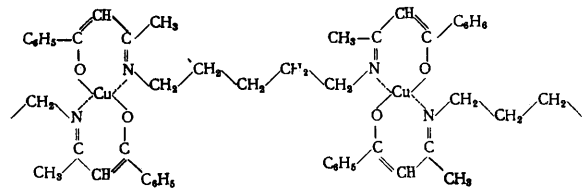
where Me = Cu^{2+}, Ni^{2+}, or Zn^{2+}. These polymers have a low molecular weight of the order of 15 000. The same result is obtained if the polycoordination is carried out by heating a mixture of equimolecular quantities of the metal acetylacetonate and the bis-α-thiopicolylamide in vacuum.

The bis-α-thiopicolylamide polymers prepared from p-diaminobenzophenone and p-diaminodiphenylsulphone are the most stable thermally. The polychelates of Cu^{2+} and Ni^{2+} are stable up to 300°, and the Zn^{2+} polychelate is stable up to 370°, the loss in weight at this temperature being less than 3.5%. The higher thermal stability of the zinc-containing polymers is due to zinc having only one state of oxidation. Metals of variable valency may be oxidised on heating, and the resulting oxides probably catalyse the thermal decomposition.

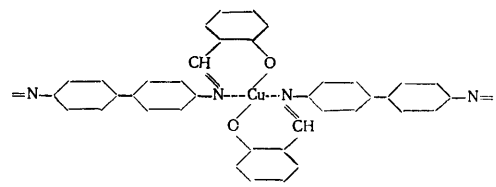
Kanda and Saito[73] have prepared high-molecular stable polychelates from 1,6-dihydroxyphenazine and Cu^{2+}, Fe^{3+}, Hg^{2+}, and Ag^{+}:



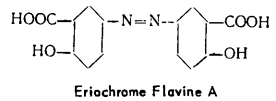
Resinous products have been obtained by reacting bis--benzoylacetone-pentamethylenediimine or bis-benzoylacetone-2,2'-diimine-diethylamine[76]:



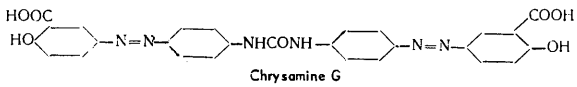
The Cu^{2+} chelates synthesised by Pfeiffer[77] from the Schiff's bases obtained from salicylaldehyde and m-phenylenediamine, p-phenylenediamine, benzidine and 1,4-diaminonaphthalene probably belong to this class of polymer. Pfeiffer gave these complexes a cyclic dimeric structure, but from their properties it may be assumed that they are polymeric[78]:



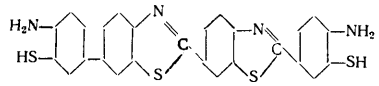
This type of polymeric chelate probably also includes the lakes formed by certain dyestuffs with metal salts, for instance:



Eriochrome Flavine A



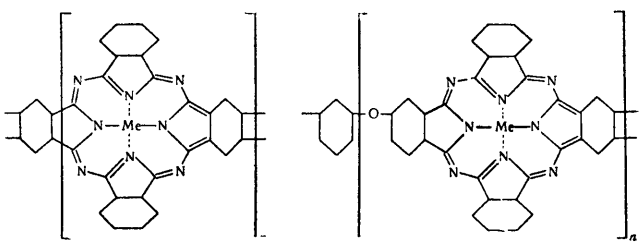
Chrysamine G



*Direct fast yellow ZKh

These lakes have not been considered from the point of view of polymer chemistry, but their structure and their ability to form complexes with salts of metals (Cr, Cu, Al, Fe) indicate that they are polymeric compounds[79].

The synthesis of polymeric phthalocyanines is of great theoretical and practical interest. The first attempts to prepare polymeric phthalocyanines from 3,3',4,4'-tetracyanodiphenyl and ions of metals of variable valency were made in 1952. Somewhat later Bailar and Drincard (cf. Marvel and Rassweiler[80]) obtained polymeric phthalocyanines from pyromellitic acid and urea, but their lack of solubility hindered the study of the polymers. In 1958 Marvel and Rassweiler[80] attempted to prepare polyphthalocyanines from pyromellitic acid, phthalic anhydride, and urea, and from 3,3',4,4' tetracarboxydiphenyl ether, phthalic anhydride, and urea:



With equimolecular properties of the reactants, linear polyphthalocyanines were obtained. The reaction mixture was heated at 170°–200° with cuprous chloride with and without ammonium molybdate as catalyst; the reaction product was a mixture of the phthalocyanine and its polymer, the presence of the catalyst decreasing the yield of polymer. The polymers are soluble in dimethylformamide and are precipitated from it by chloroform. The products are blue-green to greenish-black powders completely stable to heat, but slowly decomposing in air above 350°. They burn with difficulty, a property which leads to errors when analysing for carbon and hydrogen.

Developing the synthesis of polyphthalocyanines, Marvel and Martin[81] studied the fusion of 3,3',4,4'-tetracyanodiphenyl ether, phthalonitrile and cupric chloride in various proportions at 275° for 3 h; the products are dark blue hygroscopic powders with a metallic lustre. The sulphuric-acid solutions are brown or red-brown, as opposed to the blue sulphuric-acid solutions of copper phthalocyanine. The infra-red spectrum of these polymers shows three bands identical with those of copper phthalocyanine.

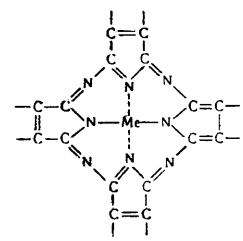
Heating a mixture of 3,3',4,4'-tetracyanodiphenyl ether with a copper salt at 275° for 3 h gives a product of very low viscosity. Increasing the reaction time leads to the formation of a three-dimensional product insoluble in sulphuric acid.

The condensation products of phthalonitrile with 3,3',4,4'-tetracyanodiphenyl ether, which are soluble in sulphuric acid, are converted into insoluble products by fusion with *p*-phenylenediamine.

All the polymeric phthalocyanines prepared by these workers decompose at 350° in air within 24 h.

Recently Berlin, Matveeva, and Sherle[82] discovered a new type of polymeric chelate, consisting mainly of carbon, nitrogen, and metal, prepared from tetracyanoethylene and metals or their compounds. On reacting 1 mole of copper acetylacetonate with 2 moles of tetracyanoethylene in a vacuum at temperatures of 160° to 300°, complex formation takes place with the liberation of acetylacetone. The product is an infusible black polymer, insoluble in organic solvents, alkalis, and dilute acids, and not decomposed by the latter.

The infra-red spectrum of a sample of the polymer did not show any intense absorption bands in the region 700–3000 cm^{-1}, except for a band at 2224 cm^{-1} corresponding to the CN group. The absence of absorption bands in this region is apparently due to the formation of polymers of a parquet structure,



Samples of the polymer show broad electron-paramagnetic-resonance lines of high intensity, with a distance between the maxima of 500–700 oersted.

The reaction of an equimolecular mixture of copper acetylacetonate, tetracyanoethylene, and phthalonitrile forms a copolymeric complex, probably of ribbon structure.

Berlin and Matveeva[83] have prepared polymeric chelates from newly synthesised polyaminoquinones. The reaction of polybenzidinodichloroquinone, prepared by condensing equimolecular quantities of chloraniline and benzidine in the presence of sodium acetate, with salts of metals (Cu, Fe, Cd, Mg, etc.) gives polymers containing 6–15% of the metal. The copper-containing polymer gives a narrow signal in its electron-paramagnetic-resonance spectrum with the *g*-factor of a free electron without hyperfine structure. In addition to the narrow signal, there is a broad symmetrical line with strong absorption in zero field. The samples of the complex possess a high magnetic susceptibility: $\kappa = 3.4 \times \times 10^{-6}$ cgs units.

This review shows that the existing data are insufficient to give a complete description of the mechanism of formation or the physico-mechanical properties of these polymers; nevertheless their structural features and the unlimited possibilities for the synthesis of various types of

* This may be better known as Immedial Yellow G G (Ed. of Translation).

polymeric chelates can lead to the preparation of new materials with a wide range of properties, occupying an intermediate position between metals and non-metallic substances.

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NON-BENZENOID AROMATIC COMPOUNDS AND THE CONCEPT OF AROMATICITY

M. E. Vol'pin

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INTRODUCTION

The structure of aromatic compounds and the causes of their special aromatic properties became one of the fundamental problems of theoretical organic chemistry almost from the moment that A. M. Butlerov put forward his theory of chemical structure.

The cyclic structural formula for benzene proposed by Kekulé and advances in synthetic organic chemistry enabled a vast range of benzene derivatives, termed "aromatic compounds", to be isolated. The concept of "aromatic compounds" was very soon extended to derivatives of naphthalene, anthracene, and other fused-ring systems. It was subsequently found that numerous heterocyclic compounds – derivatives of furan, pyrrole, thiophen, pyridine, etc. – also possess a number of properties in common with benzene derivatives and distinguishing these compounds from other heterocyclic systems.

A number of properties appeared by that time to be common to aromatic compounds:

1) Ease of formation of aromatic rings in the most varied reactions.
2) Stability of aromatic systems, and in particular the difficulty of effecting addition reactions at the multiple bonds.
3) Ease of replacement of hydrogen by various groups in electrophilic-substitution reactions (nitration, sulphonation, halogenation, acetylation, alkylation, mercuration, etc.)
4) Characteristic properties of certain substituents in aromatic systems (acidic properties of aromatic hydroxyl, weakened basicity of amino group, stability of diazo compounds, ability to undergo azo coupling, lack of reactivity of halogen, etc.).

These properties taken together, were often denoted as "aromatic properties" or "indications of aromatic character", and were also the chemical criterion of aromaticity, on the basis of which it was determined whether substances of a given class were to be included among aromatic compounds.

In reality, however, only benzene itself is characterised by all these properties. On passing from benzene to its substituted derivatives, or still more to other aromatic systems, some of the aromatic properties become weaker or even disappear, while others are appreciably strengthened and come to the fore. Thus pyrrole and furan undergo electrophilic substitution considerably more readily than does benzene, and therefore are usually regarded as "superaromatic" systems. However, they are not very stable; they readily decompose under the action of strong acids and oxidising agents, and form addition products more readily than benzene (furan even enters into a diene synthesis reaction); from this point of view they are feebly aromatic. Naphthalene, anthracene, and other polycyclic systems are also less stable than benzene, but undergo electrophilic substitution more readily.

On the other hand, the pyridine and pyrazole systems are chemically more stable than the benzene system, and more easily give substitution products under the action of nucleophilic reagents (Chichibabin amination, hydroxylation), but undergo electrophilic aromatic substitution with considerably greater difficulty than does benzene.

Thus, even with the "classical" aromatic systems no single one of the chemical properties can serve as a strict criterion of aromaticity, the more so as many olefins and especially conjugated dienes are also capable of undergoing electrophilic substitution (sulphonation, acylation, azo coupling, etc.).

Besides the chemical properties, a number of physical properties and structural peculiarities of aromatic compounds may be noted, among which are: (1) the character of the C–C bonds, which are intermediate between single and double bonds (as is shown in particular by the values of the interatomic distances); (2) the equivalence of all carbon–carbon bonds in unsubstituted monocyclic carbocyclic systems and the equivalence of all the carbon atoms; (3) the planar or almost planar structure of the ring (it has now been shown theoretically and experimentally that the atoms forming an aromatic ring may not lie strictly in a single plane, and that slight deviations from coplanarity have little effect on the total energy of the aromatic system); (4) absorption of light at comparatively long wavelengths; (5) ready polarisability; and (6) anisotropy of diamagnetic susceptibility.

As will be shown, these physical properties and structural features are characteristic in lesser or greater degree of a wide variety of aromatic systems.

The development of quantum-mechanical ideas of the nature of the chemical bond and the progress of organic synthesis during the past two decades have produced not only a considerable change in our ideas as to the nature of aromaticity and its peculiarities, but also a considerable extension of the range of systems which can be regarded as

aromatic. Compounds which are quite different in composition and properties from the "traditional" aromatic derivatives of the benzene series can be included among aromatic compounds, such as organic anions (cyclopentadienyl anion), organic cations (tropylium, cyclopropenylium, phenalenylium), dipolar compounds (azulenes, sydnones), organometallic compounds (ferrocene and other "cenes"), and finally even some inorganic compounds (borazoles, phosphoronitrile halides). Further, progress in theoretical organic chemistry has enabled the possible existence of a number of other, as yet unknown, aromatic systems to be predicted. The characteristic properties and structure of various non-benzenoid aromatic systems will be considered below, starting with carbocyclic systems.

Work on systems which are formally analogous to benzene, and in which aromatic properties are therefore to be expected, has been especially significant in the development of the structural theory of aromatic compounds. These researches are considered in the sections concerned with the so-called pseudoaromatic compounds – cyclobutadiene, cyclooctatetraene, pentalene, heptalene.

Fourteen years have elapsed since the publication in "Uspekhi Khimii" of a review on non-benzenoid aromatic systems[1]. Since that time this field of organic chemistry has undergone such an intensive development that a revision of its fundamental theoretical principles has been required. Later foreign reviews[2,3] are far from complete; furthermore, in the few years which have elapsed since their publication much new material has appeared which is of fundamental importance.

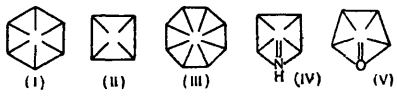
STRUCTURE OF AROMATIC COMPOUNDS AND NATURE OF AROMATICITY

The vigorous development of the chemistry of aromatic compounds at the end of the nineteenth and the beginning of the twentieth centuries led to a large number of hypotheses as to the structure of benzene and multinuclear aromatic compounds. The majority of them are now only of historic interest, and will not be considered further here (they were reviewed, for example, in 1934 [4]).

It appeared at first that the dynamic hypothesis of Kekulé[5-7] and Thiele's hypothesis of partial valencies[8,9] might form the basis of a theory of the structure of aromatic compounds. Further, the hypothesis of partial valencies enabled both unsaturated compounds, conjugated and unconjugated, and also aromatic systems, including polycyclic systems, to be considered from a single point of view.

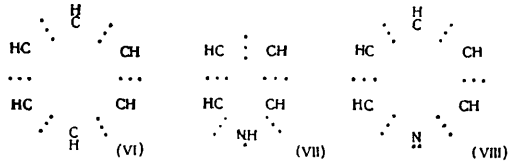
This hypothesis could not be seriously shaken even by the many cases of 1,2-addition in conjugated systems, in contradiction to Thiele's fundamental postulates. However, it received its most serious blow from the failure of Willstätter's attempt to synthesise cyclobutadiene and from the absence of aromatic properties in the cyclooctatetraene prepared by him, since it follows from the fundamental principles of this hypothesis that a simple alternation of single and double bonds in a cyclic system is the necessary and sufficient condition for its aromaticity. When this prediction of the hypothesis of partial valencies was not confirmed, a number of its supporters were compelled to accept a centric formula (I) for the structure of benzene[10].

However, acceptance of the Meyer[11] or Armstrong–Baeyer[12-14] centric formulae in fact meant only a recognition of the peculiar character of aromatic bonds, but in itself had no clear physical significance. The inadequacy of these formulae was aggravated by the fact that, like those of Kekule and Thiele, they were unable to explain why cyclobutadiene (II) and cyclooctatetraene (III) should differ from benzene (I).



As Bamberger correctly remarked[15-17], after having put much effort into defending and developing the idea of centric formulae, they can be appropriate and useful only if it is accepted as an axiom that a centric system can be stable only if it is "hexacentric", i.e. if the occurrence of the aromatic state requires six "potential valencies". In such a case, as Bamberger showed[15,16], cyclic formulae can easily be constructed also for various aromatic heterocyclic systems (cf. IV and V).

On the basis of the electronic theory of valency, Thomson, and then Kermack and Robinson, suggested for benzene and other aromatic systems formulae of the type (VI)–(VIII) containing three-electron bonds, regarding such bonds as specially stable and as engendering aromaticity[18].



However, Robinson[19] soon rejected this point of view, and came to the conclusion that "six electrons of the benzene molecule form a stable system, responsible for the aromatic character of the substance".

In spite of the apparently purely formal character of the hypothesis that six π electrons have a peculiar "magic" effect and in spite of the absence of any physical explanation, this idea proved to be very fertile. Not only did it enable a common factor to be found in the structure of benzene and aromatic heterocycles, and the absence of aromaticity in cyclobutadiene and cyclooctatetraene to be explained (although still purely formally), but it also allowed Armit and Robinson[19] to foretell the stability of systems containing the cyclopentadienyl anion. It was only considerably later, with the development of modern ideas of the quantum theory of the chemical bond, that the hypothesis of the special character of a sextet of π electrons received a physical basis.

In the 1930's a revision of valence theory from the standpoint of quantum mechanics was begun. It was natural that special attention should be paid to the quantum-mechanical examination of aromatic systems. For this purpose both of the main methods of calculation of quantum chemistry were widely used – the molecular-orbital method and the valence-bond method.

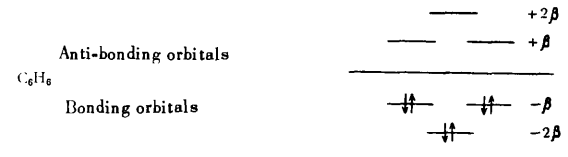
An important part in the foundation of the modern theory of aromaticity was played by Hückel[20,21], who was the first to apply the molecular-orbital method to aromatic systems. In this method the π electrons of a conjugated system are regarded as common to all the carbon atoms of the system and occur in common molecular orbitals. The number of such orbitals is equal to the number of atoms taking part in the formation of the conjugated system.

The following three types of molecular orbitals are possible: (*a*) bonding orbitals (the energy of electrons is less than their energy in the atomic orbitals, and consequently their occurrence in these orbitals makes the system more stable); (*b*) non-bonding orbitals (the energy of electrons occupying these orbitals is equal to the energy of the electrons in atomic orbitals); and (*c*) anti-bonding orbitals (the energy of electrons is greater than that in atomic orbitals, so that the occurrence of electrons in these orbitals is energetically disadvantageous).

The energy of the π electrons is often expressed in terms of so-called "resonance integrals" β, whose value is determined empirically and is usually taken to be 17–20 kcal/mole.

The numbers of bonding, non-bonding, and anti-bonding orbitals and their energies depend on the number of atoms in the system and its symmetry, and are determined by the solution of the wave equation. In conformity with the Pauli principle, not more than two electrons can be allocated to each such molecular orbital.

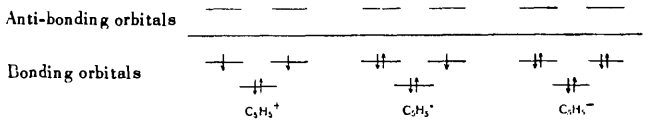
Calculation by the molecular-orbital method shows that benzene contains three bonding and three anti-bonding molecular orbitals. The energy levels are -2β, $-\beta$, and $-\beta$ for the former, and $+2\beta$, $+\beta$, and $+\beta$ for the latter (see diagram)*.



In the ground state the six π electrons of benzene occupy the most favourable, lowest energy levels, i.e. the three bonding orbitals. The energy of the π electrons consequently amounts to $2(-2\beta) + 4(-\beta) = -8\beta$. It can be shown by an analogous calculation that, in the case of three isolated double bonds, the energy of the π electrons amounts to only -6β; thus the energy of conjugation, associated with the transition of six π electrons to the common molecular orbitals, amounts to 2β.

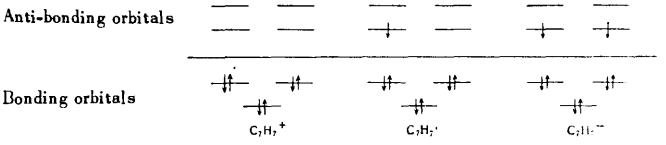
It follows even from such an elementary treatment that benzene (in the ground state) contains a stable system of six π electrons. Peculiarities of such a "closed" system of π electrons are (*a*) the absence of unoccupied positions in the bonding orbitals (i.e. entry of a new electron requires the expenditure of energy), and (*b*) all the π electrons are in bonding orbitals (i.e. the removal of any electron requires the expenditure of energy). In this respect the "closed" system of six π electrons of benzene may be compared with the specially stable electron shell of the inert gases.

The concept of a closed π-electron shell in aromatic systems was successfully applied by Hückel also to five- and seven-membered conjugated ring systems. Calculation shows that the five-membered ring C_5H_5 contains three bonding and two anti-bonding molecular orbitals. Thus the radical $C_5H_5^{\cdot}$ contains one vacancy and the cation $C_5H_5^+$ two vacancies in their bonding orbitals.



It is only in the $C_5H_5^-$ anion that all the bonding orbitals are occupied, and the six π electrons form a closed shell. Consequently, the anion should be the most stable.

Analogous considerations show that, for a seven-membered ring, possessing three bonding and four anti-bonding orbitals, the radical $C_7H_7^{\cdot}$ and the anion $C_7H_7^-$ contain respectively one and two electrons in anti-bonding orbitals, and these can therefore be easily split off; it is only in the cation $C_7H_7^+$ that all the π electrons are arranged in bonding molecular orbitals, and form a closed electron shell.



Appropriate calculation gives the conjugation energy as 2.99β for the cation $C_7H_7^+$, 2.54β for the radical $C_7H_7^{\cdot}$, and only 2.10β for the anion $C_7H_7^-$, and this anion, as the diagram shows, should occur in a triplet ground state[22].

Thus as early as 1931 Hückel had shown theoretically that not only the benzene system but also five- and seven-membered rings, possessing conjugated systems of six π electrons and bearing a negative and a positive charge respectively – the $C_5H_5^-$ anion and the $C_7H_7^+$ cation – could be aromatic and energetically stable. "It may be expected", wrote Hückel, "that a seven-membered ring will tend to lose its unpaired electron with the formation of a positively charged ion; so that a seven-membered system will behave in relation to benzene in the same way as an atom of an alkali metal in relation to an atom of the neighbouring inert gas". This bold conclusion had to wait twenty-three years for experimental confirmation by the synthesis of the cycloheptatrienylium (tropylium) cation.

The approach described frequently allows the question of the aromaticity of a wide variety of cyclic systems to be elucidated even without numerical calculations. It is found that a closed electron shell is possible in rings not only with 6 but also with 2, 10, 14, etc. π electrons. In its general form the rule derived by Hückel states that *monocyclic conjugated polyolefins having the symmetry of a regular polygon possess a closed electron shell, and consequently aromatic stability, if the number of π electrons is $4n + 2$ (where n is any integer).*

The molecular-orbital approach to the problem of aromaticity, and in particular Hückel's rule, enabled a number of deductions of importance to organic chemistry to be made:

1) For the first time a definition having physical significance was given to the concept of an "aromatic system", as a cyclic system in which all the π electrons form a single chain of conjugation and occur in bonding molecular orbitals, each of which contains two electrons.

2) The peculiar stability of the aromatic sextet of π electrons, which had been noted but not explained by classical theory, was explained as a particular case of the general rule $4n + 2$ with $n = 1$.

* Here and in subsequent calculations the energy of the π electrons in the atomic orbitals (α) is arbitrarily taken to be zero; the energy of anti-bonding orbitals is denoted by a + sign (energy of system increases when these orbitals are filled with electrons); and the energy of bonding orbitals is denoted by a − sign (energy of system diminished when electrons occupy these orbitals).

3) The aromatic character of five-membered heterocycles was explained, as these, like benzene, contain six π electrons (four electrons from double bonds and two unshared electrons of the hetero atoms) in three bonding molecular orbitals.

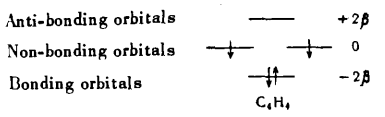
4) The aromatic character of the $C_5H_5^-$ anion and the $C_7H_7^+$ cation was predicted, which could not be done on the basis of classical structural theory.

5) Indications were obtained of the possible existence of a number of new aromatic systems. Thus, in conformity with Hückel's rule, the existence of an aromatic cyclopropenylium system could be expected with two π electrons ($4n + 2$ with $n = 0$). Comparatively simple assumptions enable the Hückel method to be applied also to elucidate the problem of new heterocyclic aromatic systems (see below). Finally, this method can be extremely fruitful when applied to various non-benzenoid polycyclic aromatic systems[22,23].

6) The molecular-orbital method enabled calculations to be made of the energies of the ground and excited states, the bond order, free valence, and the charges on atoms in aromatic systems, and thus their stability and reactivity to be characterised.

7) The molecular-orbital approach showed that cyclobutadiene and cyclooctatetraene would not be aromatic, in spite of the presence in their molecules of alternating single and double bonds[22,24-31]. Systems of this type – cyclobutadiene, cyclooctatetraene, pentalene, heptalene, etc. – have been termed, at Craig's suggestion[25], "pseudoaromatic".

The cyclobutadiene system contains four π electrons, a number which does not fit the Hückel formula $4n + 2$. Of these electrons, two are in a bonding orbital (with energy 2β), and two in two non-bonding orbitals, i.e. they have unpaired spins.



Thus the molecule would not possess a closed electron shell in Hückel's sense, and may be a diradical. The total energy of the π electrons of cyclobutadiene proves to be 4β, i.e. the same as for two unconjugated double bonds; hence the conjugation energy is zero[22,27]. In contrast to benzene, the C–C bonds should not be equivalent: calculation by the molecular-orbital method shows that the molecule should not be a square but a rectangle having sides of 1.33 Å (C=C bond) and 1.54 Å (C–C bond)[27,29,31].

In the same way, the total number of π electrons in cyclooctatetraene does not conform to Hückel's rule, and the calculated energy of conjugation (even without taking into account the lack of planarity of the eight-membered ring) does not exceed that in open-chain systems. In the eight-membered system, as in the four-membered one, an alternation of normal single and double bonds is to be expected[25,27,32].

Hence from the standpoint of the molecular-orbital method and the Hückel rule neither cyclobutadiene nor cyclooctatetraene should possess aromatic stability. This conclusion could not be derived from classical theory.

Another method of calculation used in quantum chemistry, the valence-bond (bond diagrams, localised pairs) method, has also been extremely widely applied to various aromatic systems. Further, during the first 10–15 years of existence of the two methods, the valence-bond method has been considerably more widely employed in the solution of structural problems in organic chemistry. This was due to a number of causes, including the greater descriptiveness of this method, the satisfactory results obtained for benzene and polycyclic benzenoid systems, and also the widespread use of corresponding bond diagrams by the then prevalent theory of resonance.

Applied to non-benzenoid systems, however, this method, and also the theory of resonance, yielded conclusions which were directly opposed to those resulting from the molecular-orbital method, and, as the subsequent development of organic chemistry showed, these conclusions were erroneous.

Thus the valence-bond method cannot explain the peculiar nature of a ring containing six π electrons. It is incomprehensible, why such five-membered heterocycles as pyrrole, thiophen, etc., in contrast to seven-membered heterocycles, posses an aromatic character. Finally, it is impossible to explain the aromaticity and stability of the five-membered anion $C_5H_5^-$ and the seven-membered cation $C_7H_7^+$.

Thus, for example, the explanation suggested by Wheland[33] for the acidity of cyclopentadiene (and the stability of the $C_5H_5^-$ anion) in terms of resonance theory could be equally well applied to cycloheptatriene, but the latter is known to differ markedly in this respect from cyclopentadiene, and the $C_7H_7^-$ anion is not stable.

According to the valence-bond method and the theory of resonance, cyclobutadiene is a four-membered analogue of benzene, and should possess aromatic stability[26,34-38]. Its conjugation energy should amount to 1.0 α (the value of α is approx. 32 kcal/mole), whereas that for benzene is 1.11 α: i.e. for a single π electron it should be even greater in cyclobutadiene than in benzene[35]. Cyclooctatetraene should also be aromatic according to this method and resonance theory[25], with a conjugation energy of 1.17 α, if it were planar, i.e. greater than that of benzene. Thus in 1945 Pauling wrote: "For cyclobutadiene and cyclooctatetraene the plane configuration should be stabilised as a result of resonance, but the valence angles in such plane molecules, 90° and 135°, are so far removed from the normal value that considerable strain arises; the molecules prove to be less stable and in part lose their aromatic properties"[39].

As will be shown, both these and some other conclusions regarding non-benzenoid aromatic systems made on the basis of the valence-bond method have been disproved by experimental investigations.

Thus, of the two main methods of calculation of quantum chemistry, only the molecular-orbital method gives a correct idea of the nature of aromaticity. Not only does this method enable the energy and other parameters of aromatic systems to be calculated, but also, what is especially important for the organic chemist, it often makes it possible to determine qualitatively whether a given class of compound will be aromatic.

THE CYCLOPENTADIENIDE ANION*

The five-membered ring C_5H_5 should possess a closed electron shell in the way described and should be stable in

* The suffix "ide" is widely employed at the present time to denote organic anions.

the form of the anion, which has a system of six π electrons. Calculation by the molecular-orbital method gives conjugation energies of 2.47 β for the cyclopentadienide anion $C_5H_5^-$, 1.85 β for the radical C_5H_5, and only 1.24 β for the cation $C_5H_5^+$, the last of which would occur in a diradical triplet ground state[22].

The cyclopentadienide anion forms salts with cations of the alkali and alkaline-earth metals, manganese, and the rare-earth elements. There is every reason to suppose that the bond with the metal in these compounds is ionic. Thus the close agreement between the magnetic moments found for $(C_5H_5)_2Mn$, $(C_5H_5)_3Pr$, $(C_5H_5)_3Nd$, $(C_5H_5)_3Sm$, $(C_5H_5)_3Gd$, $(C_5H_5)_3Dy$, $(C_5H_5)_3Er$, and $(C_5H_5)_3Yb$ and those calculated for the corresponding ions Mn^{2+}, Pr^{3+}, Nd^{3+}, etc. demonstrate convincingly the ionic character of the bond in these compounds[40,41]. This is confirmed also by the appreciable electrical conductivity of solutions of C_5H_5Na, $(C_5H_5)_2Mg$, and $(C_5H_5)_2Mn$ in liquid ammonia[40]. X-ray data show the salts $(C_5H_5)_2Mg$ [42] and $(C_5H_5)_2Mn$ [43] to have a pentagonal antiprism structure (like that of ferrocene).

It is impossible, in view of these results, to agree with Fritz[44], who, on the basis of a study of frequencies in the infra-red spectra of the cyclopentadienides of potassium, magnesium, beryllium, thallium, and other metals concludes that the five-membered rings in these compounds are not fully aromatic in character and that the double bonds are to a considerable extent fixed. Fritz's conclusions seem still more dubious since the spectra of these compounds do not contain any metal-carbon bond frequencies, and hence he is forced to admit that the link between the cyclopentadienyl ring and the metal is ionic. Thus, following Fritz, we would be compelled to accept the existence of a $C_5H_5^-$ ion with a charge which is to a considerable degree fixed on one of the carbon atoms in the ring, in obvious contradiction to the X-ray data (e.g. for dicyclopentadienylmagnesium, which has a sandwich structure with the magnesium atom equidistant from all the carbon atoms).

A characteristic property of the cyclopentadienide anion is its extremely high reactivity towards electrophilic reagents. Thus its salts are decomposed by water and alcohol, are carboxylated by CO_2,[45] and alkylated and arylated by alkyl and aryl halides[46]. When an alkali and chlorine (or bromine) react with cyclopentadiene all the hydrogen atoms are replaced by halogen atoms[47]: this is evidently the result of the extremely ready halogenation of the cyclopentadienide anion formed under these conditions.

The cyclopentadienide system is thus still more "superaromatic" in its reactivity than the five-membered heterocyclic systems. This conclusion is confirmed by a study of deuterium exchange in the cyclopentadienide anion, which rapidly exchanges all its hydrogen atoms for deuterium in alkaline medium, i.e. at very low D^+ concentrations[48]. Pyrrole undergoes deuterium exchange only in aqueous solutions of mineral acids (at pH $\leq$ 1)[49], and benzene slowly exchanges its hydrogen only under the action of concentrated D_2SO_4.[50] Thus the ease of deuterium exchange, the simplest electrophilic substitution, increases very markedly on passing from benzene and pyrrole to the cyclopentadienide anion.

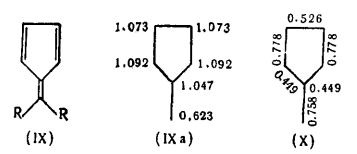
The aromatic character of the $C_5H_5^-$ anion is shown in the fact that, in spite of its high reactivity, it is nevertheless far more stable than other carbanions. As a result, cyclopentadiene and its benzo-derivatives are considerably stronger acids than other hydrocarbons (with the exception of acetylenic hydrocarbons). Whereas pK_a for diphenylmethane is 35, and for triphenylmethane 33 (in spite of the comparative stability of the triphenylmethyl anion) for fluorene it is 25, for indene 21,[51] and for cyclopentadiene not greater than 19. This value follows from the fact that potassium t-butoxide quantitatively converts cyclopentadiene into potassium cyclopentadienide[52], the value of pK_a for t-butyl alcohol being 19.

The stable cyclopentadienide anion is formed from cyclopentadiene not only by the action of alkali metals[53-55], but also in the presence of bases of moderate strength, e.g. pyridoneimine[48].

Finally, a consequence of the tendency to form the $C_5H_5^-$ anion and of the lability of the hydrogen atoms is the well known ability of cyclopentadiene to form fulvenes under the action of ketones and aldehydes in alkaline medium[56,57], to be readily mercurated with mercuric chloride in methyl alcohol[58], to undergo azo coupling[59], and to be cyanoethylated in the presence of bases (with the formation of a hexakiscyanoethyl derivative)[60].

Heterolysis of a σ C–H bond is necessary to obtain the cyclopentadienide anion from cyclopentadiene: in the fulvenes (IX), however, it is only necessary to break the more labile π bond (which requires less energy). Hence the tendency to form the cyclopentadienide system has an appreciable effect on the structure of the fulvenes and on the distribution of electron density in the ground state. This is shown primarily in the magnitude of the dipole moments of the fulvenes, which is 1.48 ± 0.03 D for dimethylfulvene, 1.34 ± 0.03 D for diphenylfulvene, etc.[61].

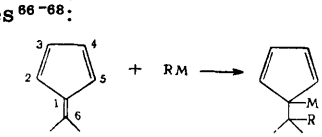
The diagram (IXa) showing the distribution of electron density, obtained by the molecular-orbital method, is also in full agreement with these experimental results (values $>>1$ indicate a negative charge, and those <1 a positive charge)[62]



(IX) (IXa) (X)

It can be seen from the diagram that the five-membered ring acquires a partial negative charge, and consequently some of the aromaticity of the cyclopentadienide anion. Consequently, there are no "purely" double and single bonds in the fulvenes, as is readily seen from the diagram of the π-bond indices (X) (for a double bond the index is 1, and for a single bond 0)* [63].

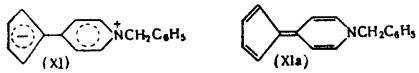
The polarity of the carbon–carbon bonds in fulvenes is shown by their ready reducibility with lithium tetrahydroaluminate[64], which distinguishes them from other hydrocarbons; this reaction involves the intermediate addition of Li^+ and H^- at the semicyclic double bond. In exactly the same way fulvenes can add on at the polar 1,6-bond organometallic compounds, e.g. phenyllithium[65] and alkylmagnesium bromides[66-68]:



The polarity of the bonds is revealed also by some other properties of the fulvenes (see, for example, the review by Bergmann[57]).

* This is equivalent to Coulson's mobile bond order, c.f. Proc. Roy. Soc., A 169, 413 (1939) (Ed. of Translation).

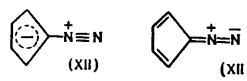
Introduction of electron-donor substituents into position 6 appreciably strengthens the aromatic character of the five-membered ring and the polarity of the fulvene molecule. This has a marked effect on the spectra, dipole moments, and reactivity[69]. Thus the dipole moment of diphenyldibenzofulvene is 1.20 D,[70] and that of bis(*p*-dimethylaminophenyl)dibenzofulvene is 3.90 D.[71] The compound obtained by Kursanov et al.[72] by the reaction of benzylpyridinium chloride with cyclopentadienyllithium is of great interest in this connection.



(XI) (XIa)

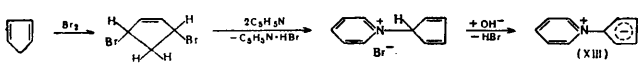
This compound can be represented by the ionic (XI) and the covalent (XIa) fulvene structures. Electrostatic forces hinder the formation of the dipolar structure (XI), but the considerable stabilisation energy of the cyclopentadienide and pyridine aromatic systems favour it. As a result, the structure of this compound is represented to an appreciable extent by formula (XI), as shown by its extremely high dipole moment of 9.7 D.[73].

The aromatic cyclopentadienide system is still more strongly stabilised when the five-membered ring is directly linked with a positively charged hetero-atom. The first example of compounds of this type (the so-called cyclopentadienylides) was obtained in 1953, when Doering and De Puy[74] prepared diazocyclopentadienylide, whose structure is more accurately represented by formula (XII) than by (XIIa).



(XII) (XIIa)

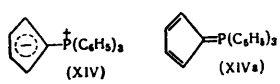
In 1955 Lloyd and Sneezum[75,76] obtained pyridinium cyclopentadienylide (XIII) by the action of pyridine on dibromocyclopentadiene followed by treatment with alkali:



(XIII)

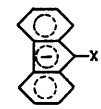
In a similar manner 4-benzylpyridinium cyclopentadienylide[77], 4-carbamoylpyridinium cyclopentadienylide, and pyridinium 2,3,4,5-tetraphenylcyclopentadienylide[76] were obtained subsequently. The distinguishing structural feature of these cyclopentadienylides is that their nitrogen atom cannot form a fifth covalent bond, and consequently the covalent fulvene structure is impossibe for them; they therefore possess an extremely high dipole moment (e.g. XIII has a dipole moment of 13.5 D)[73]. There is also a brief account of the synthesis of trimethylammonium cyclopentadienylide[79].

Triphenylphosphonium cyclopentadienylide (XIV) is also known[80]. Its dipole moment (6.99 D),[73] however, is considerably lower than that calculated for a dipolar structure (14 D); this discrepancy is associated with the fact that phosphorus, in contrast to nitrogen, can form a fifth covalent bond, owing to a vacant *d* orbital, and the substance obtained may have a structure intermediate between the "ylide" (XIV) and fulvene (XIVa) structures:



(XIV) (XIVa)

A number of analogous dipolar derivatives of the fluorenide anion (XV) are also known – the trimethylammonium (XVa), dimethylsulphonium (XVb), trimethylphosphonium (XVc), and pyridinium (XVd) derivatives[82-84].

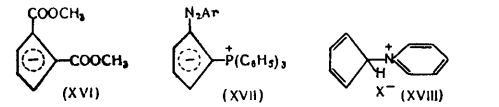


(XVa) $X=\overset{+}{N}(CH_3)_3$ (XVc) $X=\overset{+}{P}(CH_3)_3$

(XVb) $X=\overset{+}{S}(CH_3)_2$ (XVd) X= –N

The stability of the cyclopentadienide anion can be increased not only by introducing positively charged "onium" substituents but also by means of other electron-acceptor groups. Thus the 1,2-dimethoxycarbonylcyclopentadienide anion (XVI) is extremely stable. Its sodium salt is stable not only in alkaline but also in neutral solution[85].

The cyclopentadienylides are good subjects for the study of the properties of the cyclopentadienide aromatic system because of their stability. It has now been shown in a number of cases that cyclopentadienylides undergo aromatic substitution extraordinarily readily. Thus according to Kursanov and Parnes the cyclopentadienylides (XI) and (XIII) undergo deuterium exchange with enriched alcohol in alkaline, neutral, and feebly acid solutions[73]. Ramirez and Levy[86] have shown that triphenylphosphonium cyclopentadienylide (XIV) readily undergoes azo coupling with arenediazonium salts to form arylazo-derivatives (XVII).



(XVI) (XVII) (XVIII)

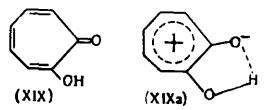
It is difficult, however, to investigate electrophilic substitutions in the cyclopentadienylides because of their high reactivity, and in particular because of the rapid entry of, not one, but several substituents with the formation of poly-substituted derivatives.

Interesting results confirming the aromatic character of five-membered rings in cyclopentadienylides have been obtained by Baranetskaya[87] and Balandin and Khidekel'[88] during the investigation of the catalytic hydrogenation of pyridinium cyclopentadienylide (XIII). Thus the velocity constant for the hydrogenation of (XIII) on a rhodium catalyst in alcoholic medium is k = 7.8 ml/min. In acetic acid, however, where as a result of addition of a proton the pyridinium cyclopentadienylide (XIII) is converted into the cyclopentadiene derivative (XVIII), the velocity of the reaction is markedly increased and k = 24.0 ml/min. These results are consistent with the general rule that the diminution in conjugation energy on passing from the aromatic to the corresponding unsaturated structure increases the rate constant for hydrogenation[88].

THE TROPYLIUM CATION

The conclusion reached by Huckel on the basis of the molecular-orbital method that the $C_7H_7^+$ cation should be stable remained for a long time without experimental confirmation. Only in 1945 was the idea of a stable seven-membered aromatic system successfully employed by Dewar[89] to explain the properties and structure of a new class of natural products, the tropolones. The properties of tropolone (XIX) and its derivatives can be explained in

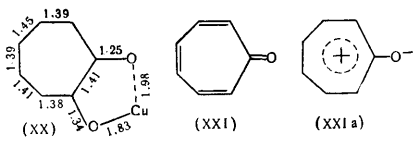
terms of a structure based on a seven-membered aromatic system (XIXa).



(XIX) (XIXa)

The chemistry of the tropolones has now grown into a vast self-contained field of organic chemistry, the number of papers on which exceeds 600. We shall not, therefore, consider the chemistry of tropones and tropolones in the present review, especially as a number of good reviews on this subject have appeared in recent years [90-94]. It will be useful, however, to describe briefly the main chemical and physical properties of these compounds which point to their aromatic character.

Like the benzene ring, the seven-membered ring in the tropolones is a planar almost regular polygon, the lengths of the carbon–carbon bonds averaging 1.40 Å. This result was obtained by Robertson [95] in an X-ray study of the copper salt of tropolone; the values found for the interatomic distances are indicated in diagram (XX).



(XX) (XXI) (XXIa)

Similar results have been obtained in an X-ray investigation of the hydrochloride and the sodium salt of tropolone [96].

Electron diffraction measurements led to the same conclusions [97], yielding the bond lengths C–C 1.39, C–H 1.10, C–O 1.34, and C=O 1.26 Å. In the tropone molecule (XXI), whose structure approximates to the dipolar structure (XXIa) with an aromatic seven-membered ring, the length of the C–C bonds is 1.41 Å.[98] Thus the values for the interatomic C–C distances in the tropolones and tropone correspond to a bond order intermediate between that of a single and a double bond, which confirms the aromatic character of these rings.

A number of physical properties of tropones and tropolones indicate the polarity of their structures, which is associated with the formation of positively charged aromatic seven-membered ring (XXIa) and (XIXa). Thus the dipole moment of tropone is 4.30 D, [99,100] whereas that of cycloheptanone is only 3.04 D.[101] Derivatives of benzotropone also have high dipole moments [102].

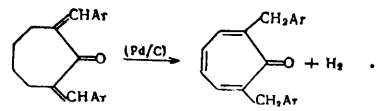
The distinguishing feature of the tropolones is the acidic character of the hydroxyl group (p*K* 7.0), which exceeds that of phenolic hydroxyl (p*K* 10.0) in acidity.

The reactivity of the tropolones also resembles in many respects that of the phenols. Tropolones readily undergo various electrophilic substitution reactions: they couple with arenediazonium salts, are nitrated by nitric acid in glacial acetic acid, sulphonated by sulphamic acid, nitrosated by nitrous acid, are readily halogenated, undergo hydroxymethylation with formaldehye in alkaline medium, and undergo the Reimer–Tiemann reaction. These reactions show the effect of the hydroxyl group and the polarised keto-group on the reactivity of the seven-membered ring. It was not possible, however, to carry out a Friedel–Crafts acylation of tropolone (possibly because of the formation of complexes with the catalyst), or to carry out its chloromethylation or its carboxylation by Kolbe's method.

On the other hand, tropolones and substituted tropones readily undergo nucleophilic substitution. Thus the methoxy group in the methyl ether of tropolone can be replaced by the radicals NHR (by the action of amines), C_6H_5 (with C_6H_5MgBr), RS (by means of RSNa), etc.

Finally, the aromatic properties of the tropones and tropolones are revealed by the ease with which they are formed from cycloheptane derivatives in the most varied reactions: bromination and dehydrobromination, dehydrogenation by means of selenium dioxide [103], oxidation with potassium permanganate [104], etc.

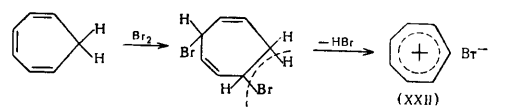
It is very interesting that palladium-on-charcoal, a highly active catalyst for the dehydrogenation of six-membered cycloalkanes, can also cause the dehydrogenation of a seven-membered ring with the formation of the aromatic tropone system [105]:



Here migration of the semicyclic double bonds into the ring and dehydrogenation occur simultaneously. As we shall see, attempts to obtain conjugated pseudoaromatic systems (cyclobutadiene, pentalene, heptalene, etc.) by the same methods were not successful.

The ease of formation of the tropolone system is consistent also with thermochemical data, according to which the conjugation energy in this aromatic system amounts to 33–36 kcal/mole.[106]

Only in 1954, some 23 years after Hückel's prediction, did Doering and Knox [52] describe the preparation of the unsubstituted tropylium cation. Tropylium bromide (XXII) was obtained by thermal elimination of hydrogen bromide from dibromocycloheptadiene according to the scheme

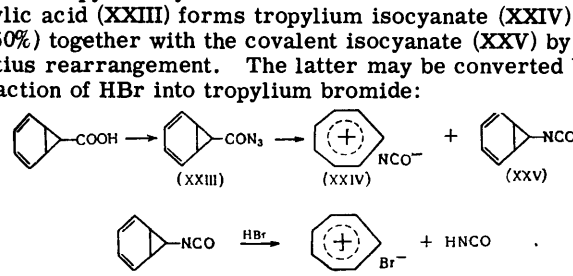


(XXII)

As early as 1891 Merling [107] had carried out the same reaction and had apparently obtained tropylium bromide. He was, however, unable to identify the compound and regarded it as a solid isomer of dibromocycloheptatriene.

Doering's method was later used to obtain salts of tropylium derivatives containing a substituent in the seven-membered ring — the bromides of carboxytropylium [108], bromotropylium, phenyltropylium, and t-butyltropylium [109].

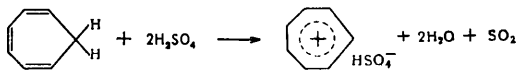
A different method, devised later by Dewar and Pettit [110,111], was based on the ready isomerisation of the norcaradiene into the tropylium system. The azide of norcaradienecarboxylic acid (XXIII) forms tropylium isocyanate (XXIV) (0–50%) together with the covalent isocyanate (XXV) by a Curtius rearrangement. The latter may be converted by the action of HBr into tropylium bromide:



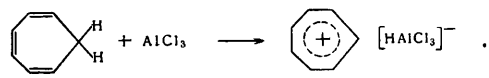
(XXIII) (XXIV) (XXV)

Methyltropylium salts are obtained similarly from the azide of methylnorcaradienecarboxylic acid.

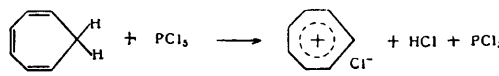
It might be expected that tropylium, as a stable aromatic system, would be readily formed directly from cycloheptatriene (tropylidene) by fission of a hydride ion from the CH_2 group accompanied by transition of the carbon atom from an sp^3 into an sp^2 state of hybridisation. Kursanov and Vol'pin have indeed shown[112] that tropylium salts are formed by the action of a wide variety of electrophilic reagents on cycloheptatriene, in spite of the fact that many of these substances react vigorously with the double bonds of the cycloheptatriene. Thus concentrated sulphuric acid converts up to 18% of the cycloheptatriene into a tropylium salt according to the scheme



The formation of tropylium in this reaction is similar to the formation of aliphatic carbonium ions by the action of concentrated sulphuric acid on saturated hydrocarbons containing a tertiary carbon atom[113]. The oxidation of tropylidene in acid medium with other oxidising agents (CrO_3, SeO_2) converts it also to a greater or lesser extent into tropylium. Although such strong Lewis acids as BF_3 and $AlCl_3$ react vigorously with the ethylenic bonds in tropylidene, in this case too the hydride ion is split off with formation of a tropylium salt:



Halides of elements of variable valency are especially effective for the conversion of cycloheptatriene into tropylium salts. Thus phosphorus pentachloride reacts extraordinarily readily with cycloheptatriene to form tropylium chloride, undergoing reduction to the trichloride in the process:



The reaction goes with an almost quantitative yield at room temperature, and can serve as a convenient method for the preparation of tropylium salts[112]. This method has been used also to obtain methyltropylium[113] and bromotropylium[114] salts.

Cycloheptatriene reacts in a similar manner with sulphuryl chloride, titanium tetrachloride, and ferric chloride[73]:

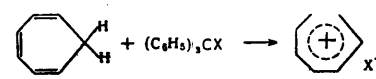
$$C_7H_8 + SO_2Cl_2 \rightarrow C_7H_7^+Cl^- + SO_2 + HCl \quad ,$$

$$C_7H_8 + TiCl_4 \rightarrow C_7H_7^+Cl^- + TiCl_3 + HCl \quad ,$$

$$C_7H_8 + 2FeCl_3 \rightarrow C_7H_7^+Cl^- + 2FeCl_2 + HCl \quad .$$

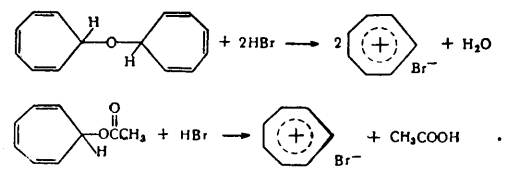
Thus, just as the action of alkali metals and strong bases on cyclopentadiene causes a proton to be split off with formation of the cyclopentadienide anion, strong Lewis acids act on cycloheptatriene to split off a hydride ion and form a tropylium cation. In both cases a non-benzenoid aromatic system containing six π electrons is formed.

Recently Dauben et al.[115] have employed yet another reaction to obtain tropylium salts by fission of a hydride ion from cycloheptatriene. They have shown that triphenylmethyl halides act on cycloheptatriene in solvents of high dissociating power to form tropylium salts:

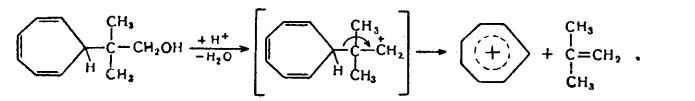


This method has given high yields (60–90%) of tropylium salts with $X^- = Cl^-$, Br^-, I^-, BF_4^-, and ClO_4^-, as well as methyltropylium, bromotropylium, and methoxytropylium salts.

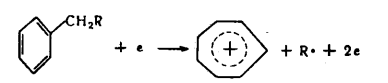
The great stability of the tropylium system is shown also by the fact that cycloheptatrienyl ethers and esters — — methoxycycloheptatriene, dicycloheptatrienyl ether[26], cycloheptatrienyl acetate, and cycloheptatrienyl benzoate[116,117] — are unusually easily cleaved by mineral acids with formation of tropylium salts, e.g.:



Vol'pin and Kursanov have recently shown that formation of tropylium may occur as a result of the rupture of carbon–carbon bonds. 2-Cycloheptatrienyl-2,2-dimethylethanol is extremely readily decomposed, even at room temperature, in the presence of acids (acetic, formic, hydrochloric, hydrobromic) or under the influence of thionyl chloride, with formation of a tropylium salt*:



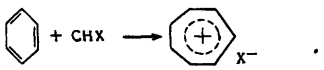
Of special interest are the few examples of direct transition from the benzene aromatic system to the tropylium system. Thus Rylander et al.[118] studied the reactions of various deuterium-labelled alkylbenzenes in the gas phase on collision with electrons in the mass spectrometer. From the distribution of deuterium in the mass spectrum of the reaction products they concluded that in all cases it is not the benzyl but the isomeric tropylium cation which is formed:



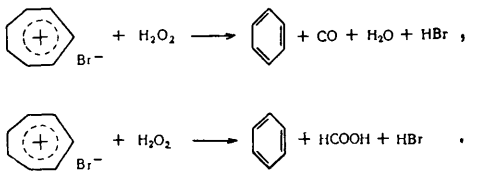
Evaluation of the energy changes in this process shows that the transition of a benzyl cation into a tropylium cation is thermodynamically probable. Such a rearrangement has not yet been observed in solution apparently because the benzyl cation (owing to the less disperse character of its charge) is stabilised by solvation to a considerably greater extent than is the tropylium cation.

* The occurrence of this type of rupture of a carbon — carbon bond has also recently been reported by Conrow [J. Amer. Chem. Soc., 81, 5461 (1959)].

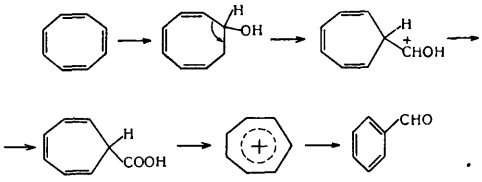
Recently Vol'pin et al.[119] have shown that benzene can be directly converted into tropylium by the action of monohalogenocarbenes, which are formed in small amounts during the reaction of CH_2Cl_2, CH_2Br_2, or CH_2I_2 with potassium t-butoxide:



Vol'pin and Kursanov[120] have discovered also the reverse reaction of the direct conversion of tropylium salts to benzene, which occurs rapidly under the influence of aqueous hydrogen peroxide and is accompanied by the formation of carbon monoxide and formic acid:



Finally, the tropylium system can be formed also by the contraction of an eight-membered ring. Thus Ganellin and Pettit[121,122] have shown that the oxidation of cyclooctatetraene to benzaldehyde occurs via the intermediate formation of a tropylium ion:



The properties and the structure of tropylium salts have attracted the continued attention of chemists[73,109].

Salts of the tropylium cation are now known with a wide variety of anions. They are solids melting at high temperatures. The majority of them (with the anions Cl^-, Br^-, I^-, BF_4^-, SiF_6^-) are readily soluble in water and are insoluble in organic solvents of low polarity; their aqueous solutions give an instantaneous reaction for the corresponding anion; tropylium chloride and bromide are extremely hygroscopic. These properties alone of the tropylium salts are sufficient to indicate the great difference between them and the alkyl halides and other organic compounds having a covalent C–X bond; in a number of their properties they resemble the salts of the alkali metals. Thus, like the K^+ cation, the tropylium ion forms a difficultly soluble (in water) perchlorate $C_7H_7ClO_4$ and a very insoluble chloroplatinate $(C_7H_7)_2PtCl_6$ and tetraphenylborate $C_7H_7B(C_6H_5)_4$. These last two salts can be employed for the analytical determination of tropylium salts in solution[123].

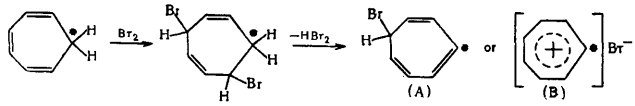
Polarographic studies have shown[123,124] that reduction of the tropylium ion begins at a very low potential (0.2 V), the character of the reduction curves being independent of the anion. A quite remarkable fact is the adsorption of the tropylium cation on the positively charged mercury surface, in spite of electrostatic repulsion. This phenomenon points to the polarisability of the π-electron cloud in the tropylium ion and indicates a similarity to benzene and other aromatic substances: these also are adsorbed on a positively charged mercury surface[125].

The existing physicochemical data for tropylium salts are in full agreement with the ionic character of the link between C_7H_7 and X and with the aromatic nature of the tropylium cation. As expected for a completely symmetrical plane seven-membered ring (D_{7h}), the infra-red spectrum of the tropylium ion contains only four strong lines, and the Raman spectrum seven, which do not coincide with the first lines. The character of these lines is similar to those of benzene and confirms the planar aromatic structure of the tropylium ion[126–138].

Theoretical examination of the electronic spectra of tropylium salts shows that they should have a weak absorption band at 4.33 eV and an intense band at 6.36 eV.[129] In close agreement with this, λ_{max} is observed at 4.51 eV ($\log\epsilon$ = = 3.64) in aqueous solutions of tropylium salts; no measurements were made at wavelengths corresponding to the second possible maximum.

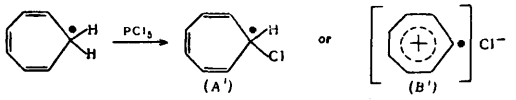
At present there are no X-ray or electron diffraction data confirming directly whether the tropylium ring is a regular heptagon. An attempt at an X-ray investigation of crystals of tropylium chloride was unsuccessful[130]; only the dimensions of the unit cell were determined. X-ray studies of the structure of tropylium perchlorate and iodide[131,132] revealed an interesting peculiarity: the tropylium ion is not completely fixed in the crystal lattice, but rotates freely in the plane of the ring (or is distributed at random about an axis perpendicular to this plane). Unfortunately this fact prevented the determination of the interatomic distances in the tropylium ring. However, a necessary consequence of its aromatic character should be the equivalence of all the carbon–carbon bonds and of all the carbon atoms in tropylium (just as in benzene).

The first direct experimental proof of the equivalence of all the carbon atoms in the tropylium ion has recently been obtained by means of labelled carbon[133]. Cycloheptatriene labelled with ^{14}C in the methylene group was converted via [^{14}C]dibromotropylidene into [^{14}C]tropylium bromide. Treatment of the product with phenylmagnesium bromide yielded [^{14}C]phenylcycloheptatriene, which was oxidised to benzoic acid.

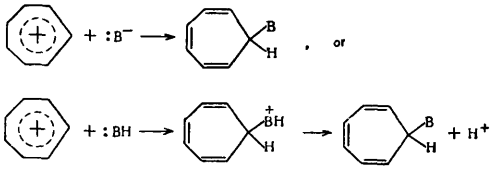


If the carbon–carbon bonds in [^{14}C]tropylium bromide were not equivalent, and if, consequently, the bromine atom were linked to one particular carbon atom (as in structure A), substitution of the bromine atom by the C_6H_5 group followed by oxidation should yield a non-radioactive benzoic acid. However, the benzoic acid was found to have a radioactivity of about one-seventh of the activity of the initial tropylium bromide. This is a consequence of the identity of all the carbon atoms (structure B) and the equal probability of attack by the phenyl group at any one of them. In another series of experiments labelled cycloheptatriene was treated with PCl_5, and the resulting tropylium salt also converted by treatment with C_6H_5MgBr into [^{14}C]phenylcycloheptatriene. Oxidation of the latter yielded a benzoic acid having the same activity (one-seventh) as in the previous case. These results also indicate the equivalence of all the carbon atoms (structure B'), since if this were not so (structure A')

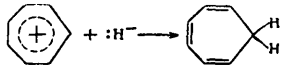
replacement of Cl by C_6H_5 should have led to the formation of a benzoic acid containing 100% ^{14}C.



The most characteristic chemical property of the tropylium salts is their ability to react with a wide variety of nucleophilic reagents according to the general scheme

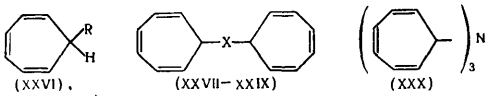


The simplest of these reactions is clearly that between tropylium and a hydride ion:



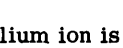
Thus cycloheptatriene is formed by the action of lithium tetrahydroaluminate or sodium tetrahydroborate (as donors of the hydride ion) on tropylium bromide. This reaction is the reverse of that described for the conversion of cycloheptatriene into tropylium salts upon reaction with electrophilic reagents.

According to Doering and Knox[52,134] tropylium salts react with CH_3O^- to form 7-methoxycycloheptatriene (XXVI), and with aqueous $NaHCO_3$ to yield ditropyl ether (XXVII). Similarly, hydrogen sulphide reacts with tropylium salts to give ditropyl sulphide (XXVIII). Aqueous ammonia forms ditropylamine (XXIX), and an ethereal solution of ammonia yields tritropylamine (XXX). Amines and acid amides react with tropylium salts in the same way: dimethylamine forms tropyldimethylamine (XXXI), acetamide gives *N*-tropylacetamide (XXXII), and succinimide yields *N*-tropylsuccinimide (XXXIII); this last compound is obtained also by the action of *N*-bromosuccinimide on cycloheptatriene[135]. The reaction of tropylium salts with potassium cyanide occurs in a similar manner and leads to the formation of 7-cyanocycloheptatriene (XXXIV).[110,111,116,134]

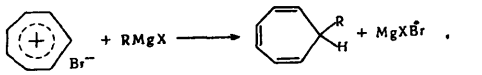


(XXVI), (XXXI – XXXIV) (XXVII – XXIX) (XXX)

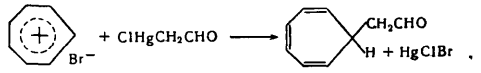
(XXVI) R=OCH_3; (XXVII) X=O; (XXVIII) X=S; (XXIX) X=NH; (XXXI) R=$N(CH_3)_2$;

(XXXII) R=$NHCOCH_3$; (XXXIII) R=  ; (XXXIV) R=CN.

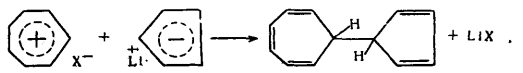
The electrophilic character of the tropylium ion is shown also in its ability to react readily with organometallic compounds. Phenyllithium or phenylmagnesium bromide reacts with tropylium bromide to yield phenyltropylidene[134], and the appropriate alkylmagnesium halides yield methyl-, isopropyl-, and t-butyltropylidenes[109].



Tropylium salts react readily with certain organomercury compounds[136], e.g.



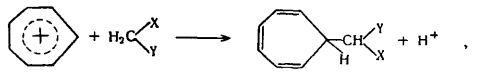
An interesting reaction occurs between tropylium salts and cyclopentadienylsodium or cyclopentadienyllithium[109, 116,117]: the salt $C_5H_5^-\ C_7H_7^+$ is not formed; a covalent compound, cyclopentadienylcycloheptatriene, is obtained, with a dipole moment of 0.6:



The formation of a covalent instead of an ionic link is intelligible if it is remembered that cyclopentadiene is an extremely weak acid.

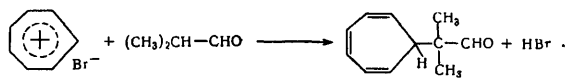
The unusually high activity of tropylium salts discovered by Vol'pin et al.[137] in alkylation reactions is associated with the "carbonium" electrophilic properties of the tropylium ion. Whereas the alkylation of compounds containing a reactive hydrogen atom with alkyl halides requires additional activation (catalysts, bases), tropylium salts react in acid medium without any activators, frequently in the cold and even with evolution of heat.

Thus tropylium salts react very readily in the cold with substances containing an active methylene group: with esters of β-keto acids (acetoacetic, diacetoacetic), β-diketones (acetylacetone, dimedone), β-dicarboxylic acids and their derivatives (malonic acid, malonic ester, cyanoacetic ester). The active hydrogen atom in the cycloheptatrienyl radical is replaced in these reactions according to the general scheme



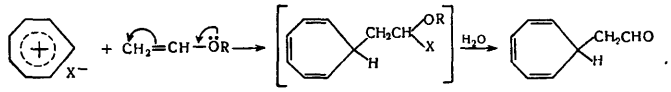
where X and Y = COOH, $COOC_2H_5$, $COCH_3$, NO_2, CN, etc.

Tropylium salts react in a similar manner with aliphatic aldehydes (acetaldehyde, propionaldehyde, isobutyraldehyde, etc.)[138], e.g.:



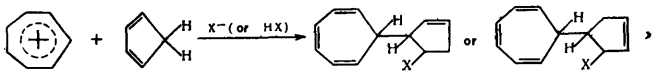
Aliphatic and alkyl aryl ketones also react with tropylium salts, but only on heating. A few aromatic compounds also react with tropylium salts — phenol, quinol, phloroglucinol, resorcinol, and α- and β-naphthols[137].

The highly electrophilic character of the tropylium ion is shown also by the fact that it readily attacks several compounds having activated double bonds[136,137]. Here activation of the multiple bond for reaction with the tropylium ion cannot be achieved solely by its conjugation with other bonds: conjugated compounds having electron-acceptor groups acrylonitrile, cinnamic acid, acrylic acid) do not react on being heated with tropylium salts. Vinyl ethers, however, readily react even in the cold[136]:



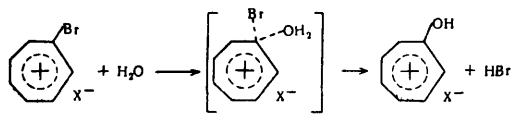
The high reactivity of the vinyl ethers is obviously connected with the supply of electrons by the oxygen and the appearance of an increased electron density at the terminal carbon atom, which is readily attacked by the tropylium cation.

An analogous phenomenon occurs in cyclopentadiene, in which the increased electron density on the C atoms is a result of the tendency to form the stable cyclopentadienyl anion. Cyclopentadiene, in contrast with other dienes, reacts readily with tropylium salts[73,137]:



where X = Br, OC_2H_5, OH, $OCOCH_3$.

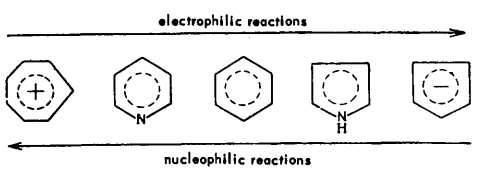
These examples show that attack of the tropylium ion by nucleophilic reagents is greatly facilitated. In the majority of cases it leads to addition of the attacking agent, but examples are also known now of nucleophilic substitution in the tropylium nucleus. Thus halogen-substituted tropylium (chlorotropylium or bromotropylium) salts on treatment with water extremely readily exchange the halogen atom for a hydroxyl group[109,114]. The mechanism of this reaction evidently involves nucleophilic attack on the tropylium nucleus by the H_2O molecule (or OH^- ion) with elimination of HBr (or the Br^- ion)[114]:



On the other hand, the tropylium system is extremely inert towards electrophilic reagents. It has not yet been possible to induce in tropylium salts any of the electrophilic reactions which are normally characteristic of aromatic systems of the benzene series — nitration, sulphonation, acylation, alkylation, etc. The ability of the tropylium system to exchange hydrogen for deuterium atoms under the influence of strong acids may be taken as a measure of the activity of the system in electrophilic substitution. Even on prolonged treatment with concentrated D_2SO_4, however, the tropylium cation does not undergo deuterium exchange[139]. Furthermore, tropylium salts do not undergo deuterium exchange even with a solution of $AlBr_3$ in liquid DBr, which is one of the strongest deutero acids[139]. Under the same conditions benzene exchanges hydrogen for deuterium almost instantaneously, and even saturated hydrocarbons undergo rapid deuterium exchange[140].

Thus, the "typical" reactions of aromatic electrophilic substitution are far from characteristic of all aromatic systems, and the tropylium system is in this respect one of the most inert.

If five-, six-, and seven-membered aromatic carbo- and heterocyclic systems are arranged in order of increasing susceptibility to electrophilic reactions (to attack by electrophilic reagents), then the series begins with the tropylium ion and ends with the cyclopentadienide anion.

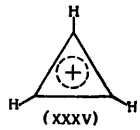


The reactivity towards nucleophilic reagents increases in the reverse order. Hence, by itself, the type of reactivity of aromatic compounds cannot serve as any strict criterion of their aromatic character.

THE CYCLOPROPENYLIUM CATION

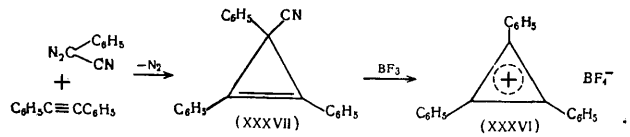
The simplest aromatic system should be the cyclopropenylium cation (XXXV) with two π electrons in the field of three nuclei. This number of π electrons conforms to the Hückel rule $4n + 2$ with $n = 0$.

Calculation by the molecular-orbital method[22] shows that the energy of conjugation is 2β for the $C_3H_3^+$ cation, β for the C_3H_3 radical, and 0 for the $C_3H_3^-$ anion.



(XXXV)

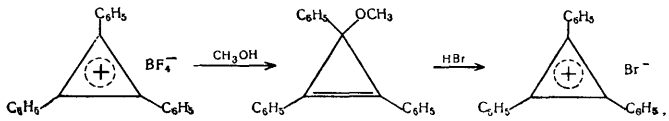
No salts of the unsubstituted cyclopropenylium cation are yet known. Recently, however, the first derivatives of this new aromatic system have been obtained. Breslow[141,142] in 1957 was able to synthesise triphenylcyclopropenylium tetrafluoroborate (XXXVI) by the series of reactions



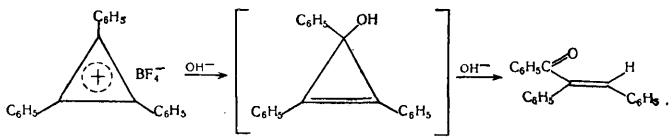
(XXXVII) (XXXVI)

The covalent 1,2,3-triphenylcyclopropenyl cyanide (XXXVII) on treatment with moist BF_3 etherate is converted into the ionic salt (XXXVI), insoluble in benzene and ether but soluble in warm acetone, methanol, and acetonitrile. The nuclear-magnetic-resonance spectrum shows all the hydrogen atoms in this compound to be equivalent, and hence that all the carbon atoms in the three-membered ring are equivalent.

Triphenylcyclopropenylium tetrafluoroborate reacts with methanol in the presence of alkali to form a covalent cyclopropenyl methyl ether, which on treatment with gaseous HBr is converted into the ionic triphenylcyclopropenylium bromide:

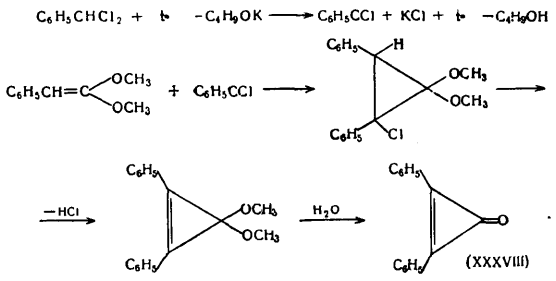


The three-membered ring of triphenylcyclopropenylium salts is opened up by reaction with aqueous alkali:

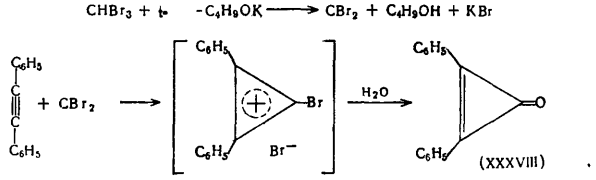


According to calculations by Bochvar at al.[143] the total conjugation energy in the triphenylcyclopropenylium cation amounts to 9.16 β; this exceeds the sum of the conjugation energies in the three phenyl groups and in the cyclopropenylium cation by 1.16 β.

A second derivative of the cyclopropenylium system obtained recently is diphenylcyclopropenone (XXXVIII). Breslow et al.[144] synthesised it starting from the acetal of phenylketen by the series of reactions



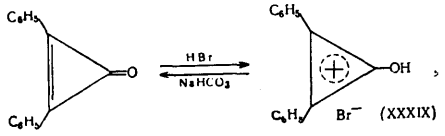
Vol'pin et al.[145] obtained this compound by addition of dichlorocarbene or dibromocarbene to diphenylacetylene:



Diphenylcyclopropenone which has a tendency to form the aromatic cyclopropenylium system is a three-membered analogue of tropone judging by its properties.

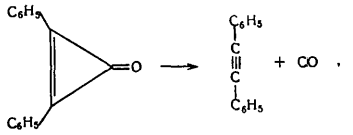
The high dipole moment of this ketone is remarkable, amounting to 5.08 D according to Syrkin and Shidlovskaya[145]. The dipole moment of benzophenone by comparison is only 2.95 D, and that of tropone itself 4.30 D.

Like tropone, diphenylcyclopropenone reacts with gaseous hydrogen chloride and hydrogen bromide to form salts[145]:

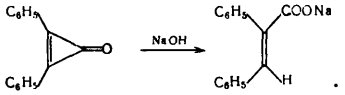


The derivative of the aromatic cyclopropenylium cation thus obtained, hydroxydiphenylcyclopropenylium bromide (XXXIX), is insoluble in non-polar solvents, but soluble in alcohol, acetone, and acetonitrile. The ionic structure of the bromide is indicated by the immediate precipitation of AgBr on addition of an alcoholic solution of $AgNO_3$, and also by the evolution of HBr by the action of concentrated sulphuric acid. On treatment of the bromide with aqueous $NaHCO_3$ it is quantitatively converted into diphenylcyclopropenone.

The stability of this ketone and the bromide is remarkable in view of the considerable angular strain, amounting in all to 180°. Only at temperatures above 130° does the ketone decompose according to the equation[144]



The three-membered ring can be opened also by heating with a solution of alkali[145]:



Even at -70° lithium tetrahydroaluminate reduces not only the carbonyl group but also the double bond of the diphenylcyclopropenone, and this is evidently also connected with the high polarity of its molecule[145].

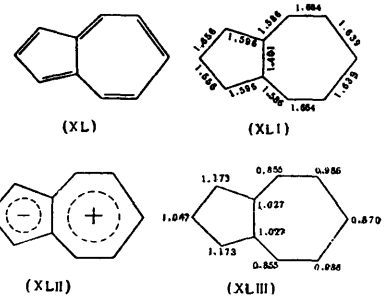
The stability of diphenylcyclopropenone, its unusually high dipole moment, and its ability to form salts with acids can be explained only by the existence of the aromatic cyclopropenylium system.

The chemistry of the aromatic cyclopropenylium system is now at the beginning of its development. The immediate task in this field should be the synthesis of salts of the unsubstituted cyclopropenylium cation and study of its properties.

AZULENES

An interesting class of non-benzenoid aromatic compounds is formed by the azulenes, which contain a fused system consisting of a five- and a seven-membered ring (they have already been reviewed[146-148]).

Pfau and Plattner[149] in 1936 established the structure of azulene as a bicyclic hydrocarbon (XL) with alternating single and double bonds. The number of π electrons in azulene (ten) is the same as in naphthalene, and obeys the Hückel rule ($4n + 2$ with $n = 2$), and there is therefore every reason to expect the azulene system to be aromatic in character.

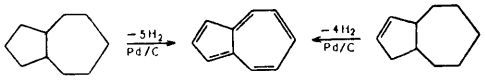


The aromatic character of the azulenes is confirmed by measurement of their heats of combustion. It was found experimentally[150] that the energy of conjugation in the azulene system is 45 kcal/mole. The value found by calculation amounts to 3.0154 β.[151] Hence the order of all the bonds in azulene is intermediate between double and single bonds (see diagram XLI).[152]

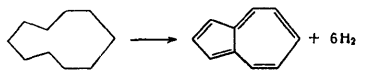
The ease of formation of the azulene system is associated with its aromatic stability. A large number of the most

varied reactions are now known in the course of which azulenes are obtained. Hydrogenated derivatives containing the azulene skeleton are readily dehydrogenated to azulene by the action of chloranil or SeO_2.

It is particularly interesting that azulenes may be successfully obtained by dehydrogenation over catalysts of the platinum group, which are so effective in the dehydrogenation of cyclohexane derivatives to substituted benzenes. Thus with palladised charcoal at 320°–335°, in conditions under which decalin is dehydrogenated to naphthalene, bicyclo[0,3,5]decane and various bicyclo[0,3,5]decenes are dehydrogenated to form azulene[153,154].



The dehydrogenation of macrocyclic hydrocarbons to form aromatic derivatives having fused six-membered rings is accompanied by the production of appreciable quantities of azulene. According to the data of Prelog[155,156], cyclodecane dehydrogenated over palladised charcoal at 350° gives a 19% yield of azulene, and cyclodecene gives a 20.8% yield.



Over activated charcoal at 420°–480° cyclodecene yields up to 60% of azulene.

Azulenes are formed also by the high-temperature (500°–600°) dehydrogenation of tetrahydrodicyclopentadiene, decalin, and perhydroacenaphthene over mixed oxide catalysts[157].

All these results confirm the aromatic character of the azulene system and its stability, which is quite comparable with that of naphthalene under the same conditions.

The π-electron cloud in the azulene molecule, however, is not symmetrical. This is a reflection of the tendency considered above for the five-membered ring to be converted into a cyclopentadienide anion, and for the seven-membered ring to change into a tropylium cation. Although such a separation of charges, represented by formula (XLII), occurs to only a slight extent (the dipole moment of azulene is 1.0 D)[61], it has a very marked effect on the physical and chemical properties of the azulenes.

Quantum-mechanical calculation of the distribution of electron density in azulene[152] confirms its dipolar structure, the charge distribution being as shown in the diagram (XLIII) (a π-electron density greater than unity indicates a negative charge on the atom, while a density less than unity indicates a positive charge). Thus all the carbon atoms in the five-membered ring carry a negative charge, while those in the seven-membered ring (apart from the atoms common to the two rings) are positively charged. From the magnitudes of the charges and taking into account the polarisability of the azulene molecule, Brown[152] concluded that electrophilic substitution will occur at position 1 in the azulenes, whereas nucleophilic and radical substitution will occur at position 4.

The "cyclopentadienide" character of the azulenes appears in the great readiness with which electrophilic substitution occurs in the five-membered ring. Azulene is considerably more reactive in such reactions than is the isomeric naphthalene. The first substituent always enters azulene in position 1, and the second in position 3.

When azulenes are nitrated with such mild reagents as copper nitrate in acetic anhydride or in tetranitromethane, 1-nitroazulene is obtained in good yield[158,159]. Nitric acid in acetic anhydride yields a mixture of 1-nitro- and 1,3-dinitroazulene[160]. Azulenes are readily sulphonated by dioxan–sulphur trioxide forming 1-monosubstituted derivatives[161]. Azulene undergoes electrophilic substitution also with *N*-bromo- or *N*-chlorosuccinimide (action of Cl^+ or Br^+), the products being 1-chloro- or 1-bromo- or else 1,3-dichloro- or 1,3-dibromoazulene[159].

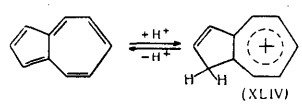
Friedel–Crafts acetylation of azulene leads to the 1,3-diacetyl derivative, but under milder conditions (acetic anhydride and $SiCl_4$ in CH_2Cl_2) it is possible to obtain 1-acetylazulene[159,160]. It is interesting that the acetyl group in 1,3-diacetylazulene readily undergoes electrophilic substitution by Cl^+ (by the action of NaOCl)[160]. Acylation of azulene with carbonyl chloride occurs under still milder conditions, in the cold and in absence of catalysts[162], the COCl group entering positions 1 and 3. 1-Acylazulenes can also be obtained by direct interaction between azulenes and carboxylic acids in the absence of catalysts[163].

The formylation of azulene occurs readily with dimethylformamide and phosphorus oxychloride (with formation of azulene-1-aldehydes)[164–166]. The halides CH_3I and CH_3Cl, methylate azulene also in position 1.[158]. The aminomethylation of azulenes, which occurs in positions 1 and 3, has also been described[167].

Azulenes also readily undergo azo coupling with arenediazonium salts with formation of 1-arylazoazulenes[168,169]. Mercuric chloride in alcohol at once precipitates a mercuration product, this reaction occurring considerably more readily than with thiophen[159].

Finally, the readiness with which electrophilic substitution occurs with azulene can be demonstrated also in the case of the simplest of such reactions, deuterium exchange. It has recently been shown[170] that azulene, like cyclopentadienylides, undergoes rapid deuterium exchange in neutral medium, only the two H atoms in positions 1 and 3 being replaced by D.

The properties of azulene as a derivative of the cyclopentadienide anion are exhibited also in the readiness with which it adds on a proton on dissolution in mineral acids to form the azulenium cation (XLIV):

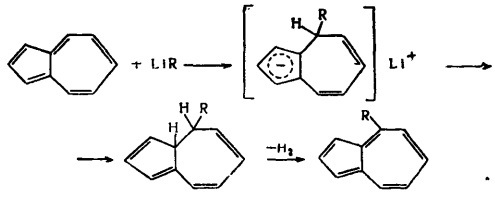


(XLIV)

In basic strength azulene approaches *o*-nitroaniline[171] (pK = 0.55 in HCOOH). On salt formation the chromophoric system of azulene breaks down, the colour changing from blue to yellow; the resulting azulenium ion is essentially a substituted tropylium ion and has an absorption maximum in the ultra-violet (λ_{max} 352 mμ), which differs markedly from the absorption maximum of the original azulene (λ_{max} 580 mμ).

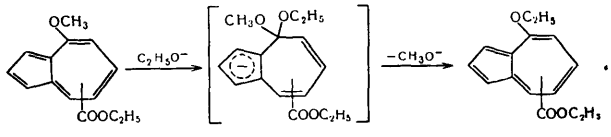
The nucleophilic reactions characteristic of tropylium salts have been considerably less studied in the azulene system. Hafner and Weldes[172,173] have shown that organometallic compounds are able to add on to the azulene molecule, the first alkyl or aryl group entering position 4, and

the second entering position 8 (i.e. the positions having the greatest positive charge):



This reaction is analogous to the addition of organometallic compounds to the semicyclic double bond in fulvenes (see above).

According to Reid et al.[174] the action of sodamide on azulene leads to nucleophilic substitution with entry of the amino group into the seven-membered ring (in position 4). However, only small amounts of the reaction product were formed, and its structure cannot strictly be regarded as proved. The occurrence of nucleophilic reactions in the azulene system is evidently complicated by its lack of stability towards bases. Thus azulene is rapidly decomposed on heating with alcoholic alkali. In the case of the more stable azulenecarboxylic acid it was possible to show that the 4-methoxy group readily undergoes nucleophilic substitution by the ethoxy group with alcoholic alkali[174]:



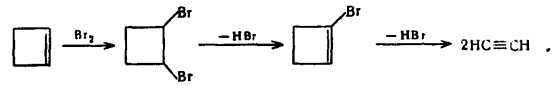
It may be expected to be possible to cause azulene and its salts to undergo many of the nucleophilic reactions studied with tropylium salts which occur in weakly alkaline, neutral, and acid media.

Thus numerous physical and chemical results confirm the aromatic character of the azulenes, which can be regarded as "tropylium cyclopentadienylides" combining the properties of the aromatic cyclopentadienide anion with those of the aromatic tropylium cation.

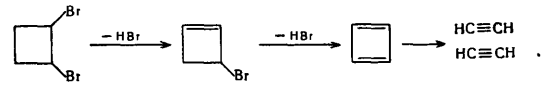
CYCLOBUTADIENE

Investigations of the pseudoaromatic systems cyclobutadiene, cyclooctatetraene, pentalene, and heptalene, which would be expected to be similar to benzene and to possess aromatic properties, serve as an especially clear example of the attempts made to verify experimentally theoretical ideas about aromaticity.

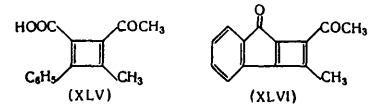
Starting from the idea of partial valencies, Willstätter and Schmädel[175] undertook in 1905 the first attempt to synthesise cyclobutadiene as a possible four-membered aromatic system. They obtained 1,2-dibromocyclobutane on adding bromine to cyclobutene, but elimination of hydrogen bromide from this material proved to be considerably more difficult than with the ordinary aliphatic dibromides. The action of quinoline on dibromocyclobutane yields a coloured polymer and small amounts of butadiene. When the dibromide is heated with alkali at 100°–105° only one molecule of hydrogen bromide is eliminated to form 1-bromocyclobutene. Elimination of the second molecule of hydrogen bromide requires heating with caustic potash to 210°, but acetylene is then formed instead of cyclobutadiene:



Discussing these results, Favorskii and Favorskaya[176] concluded that Willstätter had represented the structure of the unsaturated bromide incorrectly, and that the reaction very probably occurs with the formation of an allyl type of bromide and its conversion into cyclobutadiene, which breaks down further to acetylene:

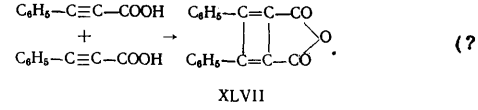


The failure of the first attempt to synthesise cyclobutadiene dissuaded chemists for a long time from studying this question afresh. Though from time to time attempts were made to ascribe the structure of a cyclobutadiene derivative to some organic compound or other, these were never based on any adequate grounds. Thus Ruhemann and Merriman[177], completely without proof, assigned the structure (XLV) to one of the reaction products formed by reaction of C_6H_5C : : C.COCl with the sodium derivative of acetonylacetone, and the structure (XLVI) to the compound derived from it.



A recent check of these results has shown that the first substance is actually 5-methyl-6-phenylsalicylic acid, and the second 2-hydroxy-4-methyl-9-fluorenone[178].

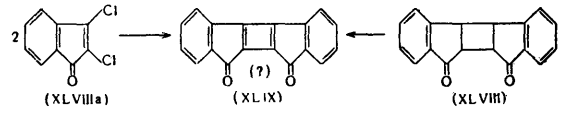
Manthey[179] and Lanser[180] suggested a substituted cyclobutadiene structure (XLVII) for triphenyltrimesic acid and its anhydride (formed from phenyltetrolic acid):



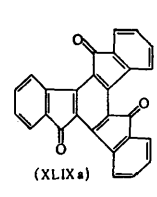
XLVII

However, it was soon established that this acid is definitely 1-phenylnaphthalene-2,3-dicarboxylic acid[181,182].

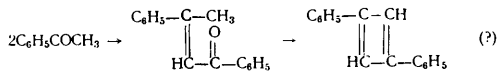
Similarly, truxinquinone, formed by the oxidation of truxone (XLVIII) or by treating dichloroindone (XLVIIIa) with copper[183],



for which the above cyclobutadiene structure (XLIX) had been proposed[180,183-185], actually proved to be a trimer of the indenylene radical s-tris(1-oxo-2,3-indenylene)benzene (XLIXa)[186-188]:



Equally unfounded was the cyclobutadiene structure assigned to one of the condensation products of acetophenone or phenylacetaldehyde in the presence of sodium ethoxide or alcoholic alkali[189,190].

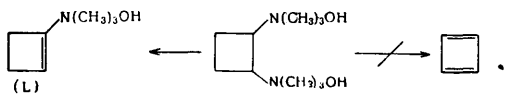


This proved to be 3,5-diphenyltoluene[191].

These examples suffice to show that special caution is necessary when authors assume, solely on the basis of their methods of synthesis and their elementary analysis, that any particular compound has a structure which includes a cyclobutadiene residue. Hitherto it has proved on checking the results only that either isomerisation or else tri(poly)--merisation has occurred in these cases, but it has never been possible to confirm the presence of a cyclobutadiene ring.

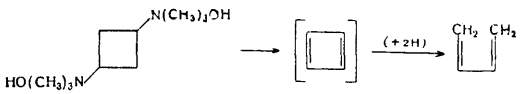
Recently, however, fresh attempts have been made to synthesise cyclobutadiene and its derivatives.

Buchman et al.[192] tried to use for this purpose the decomposition of *trans*-cyclobutane-1,2-bistrimethylammonium hydroxide:



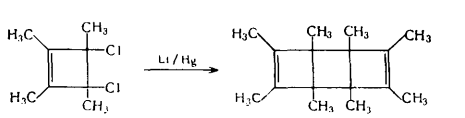
Among the reaction products were found dimethylamine, trimethylamine, *trans*-1,2-bisdimethylaminocyclobutane, and cyclobutanone, but it was not possible to detect cyclobutadiene. These workers consider that their failure is explained by the occurrence of *cis*-1,2-elimination with the intermediate formation of cyclobutene-1-trimethylammonium hydroxide (L).

To avoid 1,2-elimination, Nenitzescu et al.[193] have recently tried to obtain cyclobutadiene by the decomposition of cyclobutane-1,3-bistrimethylammonium hydroxide. They found surprisingly that, instead of cyclobutadiene, the main product was buta-1,3-diene:

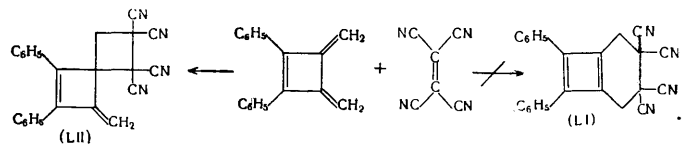


Nenitzescu considers that cyclobutadiene is first formed in the course of the reaction, and is then converted into butadiene by hydrogen abstraction from other substances present in the reaction mixture.

Similarly, the attempt of Criegee and Louis[194] to convert 3,4-dichloro-1,2,3,4-tetramethylcyclobutene[195] into tetramethylcyclobutadiene was also unsuccessful. Dehalogenation could be achieved only by the action of lithium amalgam, but then, instead of the cyclobutadiene derivative, its dimer was formed:

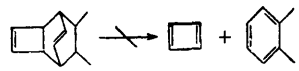


The reaction of 3,4-dimethylene-1,2-diphenylcyclobutene with tetracyanoethylene should form the cyclobutadiene derivative (LI) according to the usual pattern of diene synthesis, but unexpectedly its spirocyclic isomer (LII) is obtained instead[196]:



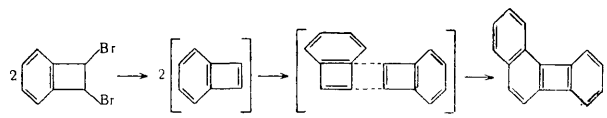
In no case in which isomerisation of some compound into a cyclobutadiene derivative could be expected (by analogy with the isomerisation of numerous compounds into benzene derivatives) did such a change occur. Thus 1,3-dimethylenecyclobutane does not pass into 1,3-dimethylcyclobutadiene. 1-Methyl-3-methylenecyclobut-2-ene readily isomerises to 1,3-dimethylenecyclobutane, but does not give a cyclobutadiene derivative[197]. Similarly, among the derivatives of cyclobutenone and cyclobutanedione no enols or enol acetates are formed corresponding to the cyclobutadiene structure[196,199].

It might be expected that the cyclobutene bridge would break away with the formation of cyclobutadiene in the pyrolysis of various adducts of cyclooctatetraene, e.g.:

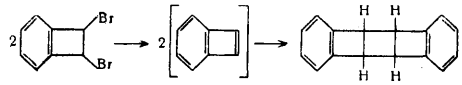


In all such cases, however, buta-1,3-diene is formed instead[193,200].

Finally, reference may be made to attempts to obtain benzocyclobutadiene, which should be more stable than cyclobutadiene itself. Treatment of 1,2-dibromobenzocyclobutene with zinc dust gave not benzocyclobutadiene but its dimer[201]:

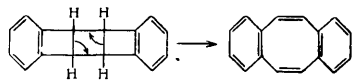


Similarly, in the dehydrobromination of 1,2-dibromobenzocyclobutene, instead of the bromobenzocyclobutadiene its dimer is formed[201]. Debromination occurs in an analogous manner even with lithium amalgam[202]. Curiously, if the same reaction is carried out in the presence of tetracarbonylnickel, a dimer with a different structure is formed[203]:



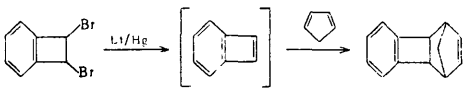
The role of the tetracarbonylnickel is apparently to form an unstable π complex with the benzocyclobutadiene formed as an intermediate, which on thermal decomposition gives the dimer.

It might be expected that pyrolysis of this dimer would lead to the formation of the monomeric benzocyclobutadiene, but it was found that at 150°–155° the dimer is converted into dibenzocyclooctatetraene[203]:

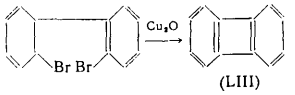


Nenitzescu et al.[202] demonstrated the formation of an unstable benzocyclobutadiene intermediate in reactions of

this type by an ingenious method. They carried out the reaction of 1,2-dibromobenzocyclobutene with lithium amalgam in the presence of cyclopentadiene (as diene component in a Diels–Alder reaction), and separated the adduct of cyclopentadiene with benzocyclobutene:



It is to be specially noted that dibenzocyclobutadiene (biphenylene) (LIII), in contrast to cyclobutadiene and benzocyclobutadiene, is a quite stable substance. After numerous unsuccessful attempts, it was obtained in 1941 by Lothrop[204] by distilling 2,2'-dibromobiphenyl or 9-iodoniofluorene iodide over cuprous oxide:



(LIII)

Subsequently biphenylene was synthesised also by the reaction of 2,2'-biphenyldimagnesium bromide with cupric chloride[205,206] and by heating *o,o'*-biphenylylenemercury with silver[207]. Substituted biphenylenes[206,208], 1,2-binaphthylene[209], and 2,3-binaphthylene[210] were obtained by an analogous method. The structure of biphenylene was confirmed by electron-diffraction[211] and X-ray[212] measurements.

The difference between cyclobutadiene and its dibenzo derivative is obviously explained by the fact that the latter is not really a cyclobutadiene derivative. It contains two benzene rings linked by sp^2-hybridised σ-bonds, as a result of which the distance between the rings is 1.46 A. The ultra-violet spectra of biphenylene[213,214] apparently indicate some interaction between the aromatic rings through the four-membered ring.

Consideration of the attempts to synthesise cyclobutadiene and its derivatives shows that it is an extremely unstable compound. The formation of cyclobutadiene is extraordinarily difficult to accomplish. Even if it is formed, it very rapidly undergoes secondary reactions. In this respect cyclobutadiene may be regarded as one of the most reactive olefines, but not as an aromatic system.

The instability of cyclobutadiene and the difference between it and benzene are most often explained by the considerable angular strain in a four-membered ring containing two double bonds. Indeed, the strain at each corner of the cyclobutadiene ring amounts to 120–90 = 30°, and that for the whole molecule to 30° × 4 = 120°. This explanation has been given by many authors hitherto both in papers on aromatic systems[1,215] and in general textbooks[216]. However, it does not stand up to serious criticism. Why, then, are biphenylene (with a total angular strain also of 120°), diphenyldimethylenecyclobutene (strain 120°), and cyclopropene (strain 169°) stable? Furthermore, the recently prepared derivatives of cyclopropenone and cyclopropenylium, with an angular strain of ~180°, have proved to be quite stable.

Knunyants et al.[217] have recently shown convincingly from an examination of published evidence that this generally accepted idea as to the difficulty of formation of four-membered rings and the instability of compounds of this type has, in fact, no sound basis. It may be concluded that the marked difference in properties between cyclobutadiene and benzene is due, not to any tension in the former system[32], but to the difference in the character of the π-electron systems of these compounds predicted by the molecular-orbital method.

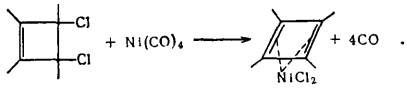
The experimental results cited show also the error of conclusions as to the aromatic character of cyclobutadiene based on the valence-bond method.

On the basis of results obtained by the molecular-orbital method for the instability of the π-electron system in cyclobutadiene and the presence in its molecule of two unpaired electrons, Longuet–Higgins and Orgel[218] suggested that cyclobutadiene should form stable complexes with the transition metals. From an examination of the symmetry of the molecular orbitals of cyclobutadiene they concluded that the two unpaired electrons, occurring in the doubly degenerate non-bonding orbital e_{1g}, could form two covalent π bonds with the metal atom. In addition, a weak coordinate σ bond between the metal and the bonding a_{1u} ring orbital and a weak σ bond with the anti-bonding a_{2u} ring orbital are possible. It follows from this that the cyclobutadiene complex will be even more stable than the cyclopentadienyl complex.

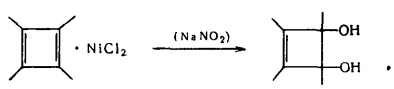
Considering the possible electronic structure of cyclobutadienyl complexes of this type, Longuet–Higgins and Orgel conclude that the formation of complexes of the type $(C_4H_4)MX_4$ is possible, with an outer shell containing 18 or 16 electrons (with complexes of neutral atoms or cations respectively), e.g. $[(C_4H_4)AuCl_2]^+$, $(C_4H_4)Ni(CN)_2$, $[(C_4H_4)\cdot Ni(CO)_2]^+$, $[(C_4H_4)Co(CO)_2]^+$, etc.

The suggestion of the possible existence of stable cyclobutadiene complexes of this kind proved to be extremely fruitful. Thus it is possible that the compound obtained as early as 1908 by Makowka[219] by passing acetylene into an aqueous solution of $PdCl_2$, which has the composition $(C_4H_4)PdCl(OH)$, is actually a cyclobutadiene complex. It is quite probable that the polymerisation of acetylene to cyclooctatetraene in the presence of $Ni(CN)_2$ occurs via the intermediate formation of the cyclobutadiene complex $(C_4H_4)Ni(CN)_2$. Such complexes may form intermediate stages in a number of other reactions of acetylene[220].

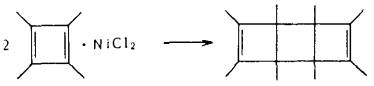
The correctness of the prediction that cyclobutadiene would form stable complexes with transition metals is provided by recent syntheses of such compounds. Criegee and Schroder[221] obtained in good yield a tetramethylcyclobutadiene complex of composition $C_8H_{12}NiCl_2$ by the action of nickel carbonyl on tetramethyldichlorocyclobutene in boiling benzene:



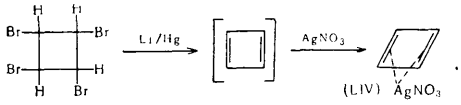
This substance forms reddish-violet crystals, soluble in water to yield a blood-red solution, and in chloroform with a violet coloration. The nuclear-magnetic-resonance spectrum of this material indicates the presence of twelve equivalent hydrogen atoms. The fact that the tetramethylcyclobutadiene is monomeric in this complex is shown by its reaction with sodium nitrite, in which a tetramethyl-*cis*-cyclobutenediol is formed which had been obtained earlier by hydrolysis of tetramethyldichlorocyclobutene:



The complex is so stable that it decomposes only at 250°, forming the dimer of tetramethylcyclobutadiene:



Avram et al.[222] treated 1,2,3,4-tetrabromocyclobutane with lithium amalgam, and separated the resulting unstable cyclobutadiene in the form of its complex with silver nitrate, which apparently has the structure (LIV):



(LIV)

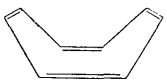
This complex is decomposed on heating with water, and the extremely unstable gas which is then evolved can again be absorbed in silver nitrate solution.

CYCLOOCTATETRAENE

The absence of aromatic properties in cyclooctatetraene is now well known and has been so widely demonstrated experimentally that we shall confine ourselves here to a brief consideration of the main results.

The chemical properties of cyclooctatetraene indicate the presence of typical double bonds in its molecule. Thus it is readily oxidised by potassium permanganate or mercuric sulphate solution, it adds on chlorine, bromine and hydrogen bromide, and also lithium and sodium, it is reduced by hydrogen on nickel, palladium, and platinum catalysts, and undergoes the Diels–Alder reaction with dienophiles (see, for example, Craig's review[223]).

Electron-diffraction and X-ray study of the structure of the cyclooctatetraene molecule also indicates the presence of alternating single and double bonds[224,225]. This agrees with the results of many spectral investigations. The spatial structure of the cyclooctatetraene molecule evidently corresponds to the symmetry D_{2d} in conformity with the "tub" or "boat" form (LV)[226–228].



(LV)

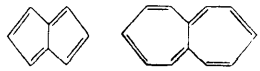
Thermochemical studies indicate the absence of appreciable conjugation in cyclooctatetraene; its heat of formation from the elements at 25° amounts to 59.07 ± 0.29 kcal/mole, and it is 34 kcal/mole less stable than the isomeric styrene[229].

Thus both the physical and chemical results are in agreement with molecular-orbital calculations, according to which the cyclooctatetraene molecule should not be aromatic[25,27,32,230], its conjugation energy should be low (not above 18.8 kcal/mole), and the molecule should contain alternating single and double carbon–carbon bonds of different lengths[27].

Cyclooctatetraene forms a dilithium derivative $Li_2C_8H_8$. According to a communication of Ubbelohde[231], not yet corroborated, the magnetic susceptibility of this compound indicates that it has the structure $(Li^+)_2(C_8H_8)^{2-}$ and is a derivative of the $C_8H_8^{2-}$ system containing ten π electrons and possessing aromatic character. In contrast to the dilithium derivative, dibromocyclooctatetraene is not a salt of the $C_8H_8^{2+}$ cation and is not aromatic.

PENTALENE AND HEPTALENE

If the nearest bicyclic analogues of azulene and naphthalene – pentalene (LVI) and heptalene (LVII) – are examined on the basis of the theoretical considerations described, it is readily concluded that, in spite of the presence of alternating single and double bonds, they should not possess aromatic properties.



(LVI) (LVII)

Pentalene contains a system of eight π electrons, and heptalene one of twelve π electrons; i.e. in neither case are conditions satisfied for the formation of a closed shell (in Hückel's sense) containing $(4n + 2)$ π electrons.

Quantum-mechanical calculations for pentalene and heptalene by the valence-bond method give quite different results. For pentalene they give a conjugation energy of 1.10 α (where $\alpha \cong 32$ kcal),[232–236] i.e. the same as for benzene; for a single π electron, however, calculation gives the same conjugation energy as in azulene.

The difference consists in the fact that, according to the valence-bond method, the wave function representing the ground state of pentalene and heptalene (and also of cyclobutadiene) is unsymmetrical relative to the symmetry axes of the molecule (it changes sign under certain symmetry operations)[25,233,234], whereas the wave functions of azulene, naphthalene, and anthracene are completely symmetrical. Craig[25] therefore suggested that cyclic molecules having a completely symmetrical ground state should be classed as normal aromatic molecules, and those having an incompletely symmetrical ground state (pentalene, heptalene, cyclobutadiene, cyclooctatetraene) as pseudoaromatic. However, Craig admits that there is no direct connection between this difference in symmetry of the wave function and the possible instability of such pseudoaromatic systems, since the valence-bond method predicts a high conjugation energy for them.

Calculations by the molecular-orbital method also indicate a considerable conjugation energy, 2.486 β (or 1.087 γ) in pentalene[232–236] and 3.61 β in heptalene[235]. A number of authors have concluded from this that these systems are stable[235,237].

Such a conclusion is, however, premature, and the above quantum-mechanical criteria of aromaticity permit different conclusions to be reached. Calculation by the molecular-orbital method gives the following energy levels for the molecular orbitals in pentalene, heptalene, and for comparison azulene (in γ units, where γ is about 42 kcal/mole)[238].

	Pentalene	Azulene	Heptalene
Anti-bonding levels			+4.7436
		+4.4003	+3.5873
		+3.5089	+3.0548
	+4.000	+2.5566	+1.3333
	+3.3180	+0.9045	+0.7985
	+2.1876	+0.4449	+0.3373
Non-bonding levels	0	—	0
Bonding levels	−0.4221	−0.4264	−0.8000
	−0.8000	−0.7260	−0.9910
	−1.0448	−1.0125	−1.0809
	−1.4775	−1.1689	−1.2087
		−1.4645	−1.4516

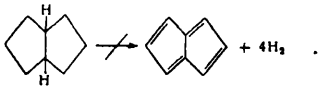
These data show that the eight π electrons in pentalene can occupy four bonding orbitals, and the ten π electrons in azulene five bonding orbitals. The nearest unoccupied level in pentalene proves to be one of zero energy, whereas in azulene, benzene, naphthalene, and all other fused benzene derivatives the nearest unoccupied level is always anti--bonding. The difference between the highest occupied and the lowest unoccupied levels is therefore comparatively low (0.4221 γ) in the case of pentalene, whereas it amounts to 0.8713 γ with azulene, 2.1333 γ with benzene, 1.2662 γ with naphthalene, 1.2388 γ with phenanthrene, etc.[238]. Since an unoccupied level of zero energy is present in pentalene, its molecule should be comparatively readily converted from the ground singlet state to an excited triplet (diradical) state, and consequently should be extremely reactive. On the other hand, the high reactivity of pentalene is due also to the fact that its molecule can accept a pair of electrons into an unoccupied non-bonding level and can therefore react readily with various nucleophilic reagents.

In heptalene ten of the twelve π electrons are in bonding levels, and two in a non-bonding level of zero energy. Consequently, it may be expected that the heptalene molecule will readily give up its electron pair under the influence of even weak nucleophilic reagents.

It may be concluded that the π-electron systems of pentalene and heptalene are not "closed", since they can readily either acquire (pentalene) or give up (heptalene) π electrons without appreciable consumption of energy. The case of pentalene and heptalene shows very clearly that the stability of an aromatic system is determined not only by a high conjugation energy of the π electrons but also by the way in which its molecular orbitals are filled (the "degree of completion" of the electron shell). Other examples supporting this thesis are the cation $C_5H_5^+$, for which the energy of conjugation is 1.24 β, and the anion $C_7H_7^-$ with a conjugation energy of 2.83 β. However, the former has one unoccupied bonding electronic level, and the latter contains two electrons in anti-bonding levels. Both these systems, therefore, in spite of their high conjugation energy, are unstable and are not aromatic. The abundant experimental data resulting from the numerous attempts to synthesise the pentalene and heptalene systems confirm the above conclusion as to their non-aromatic character.

The question of the existence of pentalene as a possible aromatic system was first raised by Armit and Robinson[239]. Subsequently, based on Robinson's idea of the necessity of a sextet of π electrons in aromatic systems, they expressed doubt about the possible aromaticity of pentalene[19].

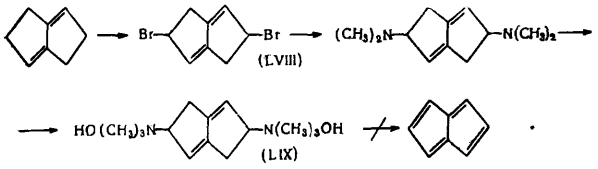
The formal analogy between pentalene and naphthalene, led Barrett and Linstead[240] to suggest that pentalene might be obtained by the dehydrogenation of *cis*-bicyclo[0,3,3]octane, since naphthalene is readily obtained by the dehydrogenation of decalin:



However, *cis*-bicyclo[0,3,3]octane remained unchanged at 300°–320° over platinised asbestos. Similarly, 2-benzylidene-*cis*-bicyclo[0,3,3]octane could not be dehydrogenated in the liquid phase by means of selenium[241].

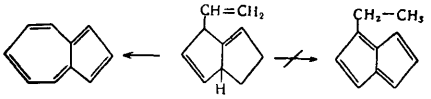
The attempted catalytic dehydrogenation of tetrahydropentalenes also failed[242]. When a mixture of them was passed over platinised asbestos at 360°–380° or over platinised charcoal at 320°–340° they remained practically unchanged, although under the same conditions tetralin is almost quantitatively converted to naphthalene. Attempts to convert tetrahydropentalene to pentalene by successive halogenation and dehydrohalogenation also proved unsuccessful[242].

Blood and Linstead[241] studied various routes to pentalene or its derivatives. Thus by the action of *N*-bromosuccinimide on tetrahydropentalene the dibromide (LVIII) was obtained, and was converted further into the bisquaternary ammonium base (LIX). Cleavage of this by Hofmann's method, however, yielded only a resin instead of pentalene:

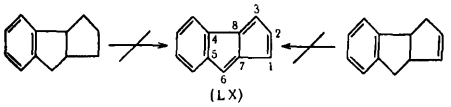


Finally, attempts by the same workers to dehydrogenate tetrahydro-1,4-dimethylpentalene to 1,4-dimethylpentalene over palladium black or palladised charcoal also ended in failure.

Vinyltetrahydropentalene when passed over palladised asbestos likewise is not converted into the substituted pentalene, small quantities of azulene only are formed[243]:

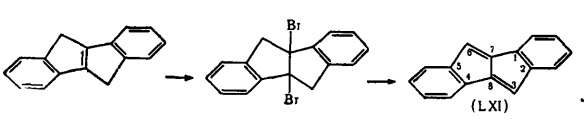


The attempted catalytic dehydrogenation of the hexahydro or the tetrahydro derivative to obtain benzopentalene (LX) was just as unsuccessful[244,245]:



Nor was it possible to dehydrogenate 4,5-dihydro-3,6--diphenylbenzopentalene, although the most varied methods were used (catalytic dehydrogenation, action of chloranil, dehydroindigo, sulphuryl chloride, lead tetraacetate, selenium dioxide, bromination with *N*-bromosuccinimide followed by dehydrobromination, etc.)[246]. An analogous attempt to obtain 4-methyl-6-isopropylbenzopentalene also ended in failure[247].

In 1952 Blood and Linstead[248] prepared 1,2:4,5-dibenzopentalene (LXI), in which the pentalene system is stabilised by two benzene rings; they obtained it by heating the bromination product of 3,6-dihydrodibenzopentalene with silver acetate:

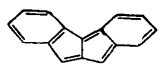


The properties of this compound clearly point to the absence of aromatic character in the pentalene system. Dibenzopentalene is rapidly hydrogenated at room temperature in the presence of palladised charcoal with the formation of

tetrahydrodibenzopentalene, it is reduced by sodium amalgam in alcohol to 3,6-dihydrodibenzopentalene, it is readily polymerised in solution in the presence of catalytic amounts of acid, it vigorously adds on a molecule of bromine, and very readily undergoes ozonisation at the 6,7 and 3,8 bonds. Thus the chemical behaviour of dibenzopentalene is like that of conjugated dienes.

In contrast to pentalene (LVI), the stabilised 1,2 : 4,5--dibenzopentalene system (LXI) is formed comparatively easily, and its numerous 3,6-derivatives have been known for a comparatively long time[249-260], having been obtained mainly by Brand and his collaborators[250-260]. All these compounds, like the unsubstituted dibenzopentalene, display the properties of typical olefins.

Attempts to synthesise 1,2 : 5,6-dibenzopentalene (LXII) have been unsuccessful[261], although calculation suggests that its conjugation energy should have almost the same value (110 kcal/mole) as the 1,2 : 4,5-isomer (120 kcal/mole)[236].



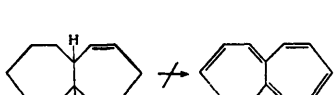
(LXII)

The following conclusions can be drawn from synthetic studies in the chemistry of pentalene:

1. Pentalene and its benzo and dibenzo derivatives, in contrast to naphthalene and azulene, are not obtained by the catalytic dehydrogenation of the corresponding di-, tetra-, hexa-, or octahydro derivatives.
2. In a wide variety of attempts to synthesise pentalene and benzopentalene by successive introduction of double bonds into the ring only polymerisation products were formed.
3. In cases in which bicyclic ketones could form the pentalene double-bond system by enolisation, such enolisation does not take place.
4. The central double bonds in dibenzopentalene display the properties of conjugated double bonds, not those of aromatic bonds.
5. In contrast to azulene, neither pentalene nor its derivatives are encountered among natural products.

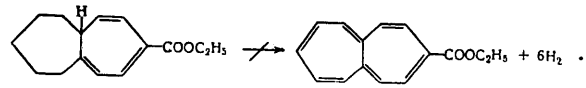
In conclusion, we may briefly consider the attempted synthesis of heptalene. The possibility that heptalene was an aromatic system was first raised by Baker[1], who in 1945 concluded, on the basis of incorrect views as to the nature of aromaticity, that the heptalene system should possess aromatic stability. The error of this conclusion is evident both from the preceding theoretical discussion and from the results of attempts to synthesise heptalene and its derivatives experimentally.

Thus an attempt at the catalytic dehydrogenation of decahydroheptalene (LXIII) over palladised charcoal at 310°--330° (in a vacuum, at 4 mm Hg) was unsuccessful[262]:

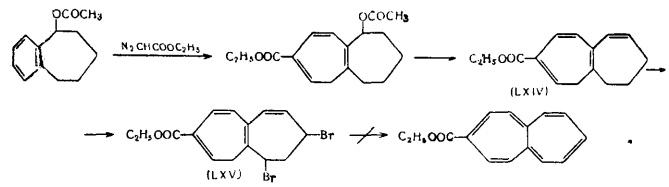


(LXIII)

Similarly, it proved impossible to obtain a substituted heptalene from the ethyl ester of bicyclo[5,5,0]dodeca-1,3,5--triene-3-carboxylic acid by liquid-phase dehydrogenation or by passing it over palladised charcoal in the vapour phase[263]:



The possibility of obtaining the heptalene system by successive introduction of double bonds was investigated[262], the following reactions being carried out:



The tetrahydroheptalene derivative (LXIV) yielded the dibromide (LXV) by the action of two molecules of *N*-bromosuccinimide, but on dehydrobromination of (LXV) with the most varied agents, rearrangement occurred with formation of substances containing a benzene ring.

Thus it has never been possible to synthesise heptalene or its derivatives, which indicates their instability and the absence of aromatic character in the heptalene system.

POLYCYCLIC SYSTEMS. GENERALISED HÜCKEL RULE

In the discussion of the azulene, pentalene, and heptalene systems, it is useful to consider the general question of the applicability of Hückel's rule to bicyclic and polycyclic systems.

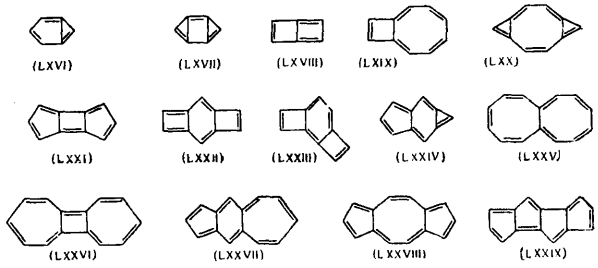
The criterion of a closed electron shell as a necessary condition for aromatic behaviour is applicable to any cyclic system. The rule for the stability of a system of $(4n + 2)$ π electrons, however, was derived by Hückel only for monocyclic molecules. Examination of numerous experimental results shows it to be applicable also to bicyclic fused systems. This is readily understood if it is assumed that the central, bridging bond introduces no appreciable change in the aromatic character of the system and is necessary only to maintain coplanarity. Such a simplification is the more admissible in that, as calculation shows, the "perturbation" caused by the central bond in naphthalene and azulene is in fact not too great and cannot affect the general aromatic character of the system.

If the bridge bond is neglected, naphthalene and azulene are derivatives of a ten-membered cyclic hydrocarbon, cyclodecapentaene, containing ten π electrons (i.e. $n = 2$ in the Hückel formula $4n + 2$) and therefore aromatic. Pentalene can be regarded as a derivative of cyclooctatetraene having eight π electrons, and heptalene as a derivative of dodecahexaene having twelve π electrons, and therefore aromatic properties can be expected to be absent from them. This rule can be extended also to a number of polycyclic systems. Thus anthracene and phenanthrene have fourteen π electrons, and as derivatives of a fourteen--membered ring they should be aromatic according to the Hückel rule (with $n = 3$), etc.

In its general form the rule can be stated as *any plane (or nearly plane) fused system containing no atoms common to more than two rings will be aromatic if the number of* π

*electrons in it is equal to 4n + 2 (where n is a whole number)**.

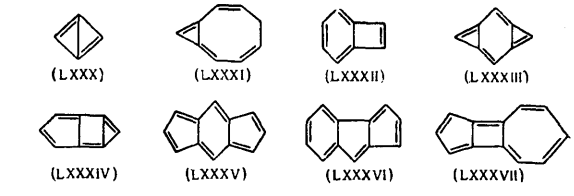
According to this generalised rule, aromaticity may be expected in the following as yet unknown systems: (LXVI)–(LXVIII), in which $n = 1$; (LXIX)–(LXXIV), where $n = 2$; and (LXXV)–(LXXIX), where $n = 3$:



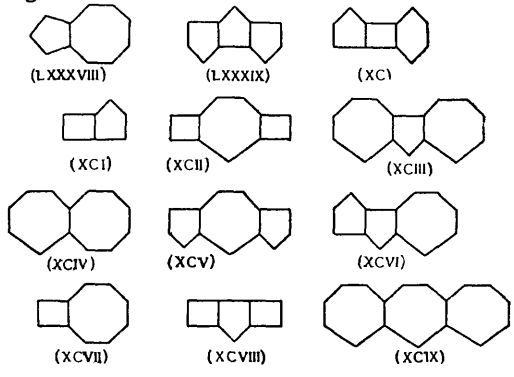
In each individual case, of course, the possibility must be taken into account of a reduction in stability due to the considerable angular strain, e.g. in (LXVII), and due to the possible non-coplanarity of eight-membered rings, e.g. in (LXXV).

Calculations have been made for the systems (LXVI), (LXVIII), and (LXXVI) which confirm the above qualitative conclusion; the conjugation energy for these systems is 2.39 β, 1.66 β, and 4.51 β respectively[22]. It is remarkable that aromaticity may be expected in fused systems composed of two cyclobutadiene (LXVIII), two cyclooctatetraene (LXXV), and two pentalene (LXXIX) residues.

From the same generalised rule, aromatic stability may be expected to be absent from the as yet unknown systems (LXXX)–(LXXXVII):



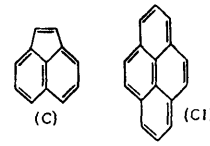
Finally, it follows from the generalised rule that the systems (LXXXVIII)–(XCIII) will be stable in the form of singly charged cations, and systems (XCIV)–(XCIX) in the form of singly charged anions**:



* This rule obviously relates only to systems in which the bridge contains no additional atoms (in the Baeyer nomenclature, to systems containing a zero-atom bridge).

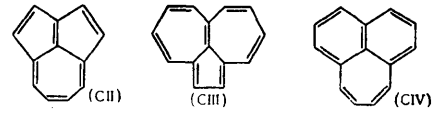
** Here and in formulae (CV)–(CVIII), for the sake of simplicity, only the carbon skeletons of the aromatic systems are indicated.

Matters are more complicated with tri- and polycyclic systems having atoms which are common to three rings. The rule of $(4n + 2)$ π electrons no longer operates with such systems. Thus, for example, the acenaphthylene (C) and pyrene (CI) systems have twelve and sixteen π electrons respectively, i.e. they do not conform to the formula $4n + 2$, although they are aromatic.

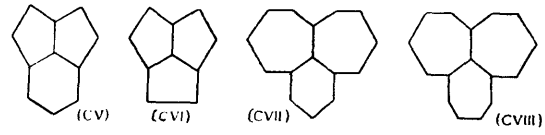


It is obviously necessary to carry out a calculation by the molecular-orbital method for each system to determine the numbers of bonding, non-bonding, and anti-bonding levels and thus to learn whether the molecule contains a closed π-electron system.

This type of calculation was carried out by Dyatkina and Shustorovich[23,264] for a number of tricyclic fused systems composed of five-, six-, and seven-membered rings, including some containing the pentalene and heptalene systems.



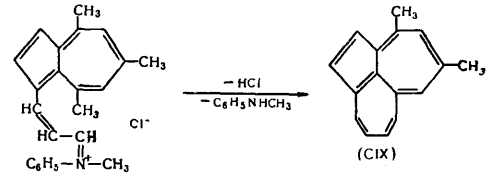
It was found that systems (CII)–(CIV) should possess aromatic stability, since the first has six bonding orbitals with a total of twelve π electrons, while the second and third have seven bonding orbitals and fourteen π electrons. Systems (CV) and (CVI) each have six bonding orbitals and eleven and ten π electrons respectively:



They should be stable in the form of the respective singly and doubly charged anions containing twelve π electrons.

Similar reasoning leads to the conclusion that the system (CVII) (seven bonding orbitals and fifteen π electrons) will have a tendency to change into the singly charged cation, whereas system (CVIII) (seven bonding orbitals and sixteen π electrons) will change into the doubly charged cation.

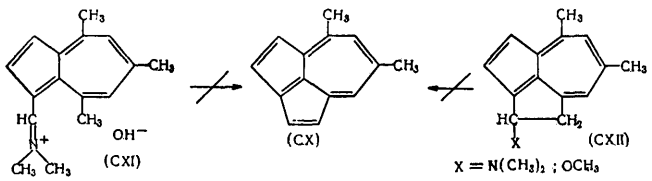
The results of this calculation by the molecular-orbital method have recently been confirmed experimentally. Hafner and Schneider[265] have synthesised the derivative (CIX) of one of the systems (CIII) calculated by Dyatkina and Shustorovich[23]:



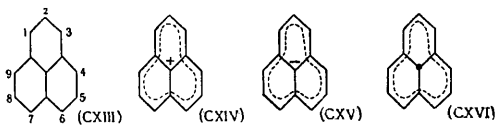
This compound proved to be quite stable. Like azulene, it dissolves in 50% sulphuric acid (with a red coloration) and is precipitated from these solutions with water, it readily

undergoes electrophilic substitution (Friedel–Crafts acetylation, and formylation), and its spectrum is similar to that of azulene. None of these results is consistent with Hafner and Schneider's view that the substance they have obtained is a heptalene derivative. Judging from its properties, it is rather an azulene derivative, in which the positive charge occurs in both seven-membered rings.

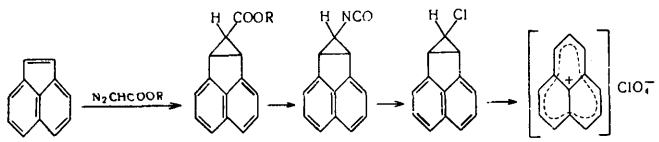
The analogous azulene derivative containing two five-membered rings (CX) should also be stable according to calculation[23], but it has not yet been possible to obtain it by cyclisation of the corresponding ammonium salts (CXI) or by introducing a double bond into 1,8-cyclopentenoazulene (CXII)[266]:



Finally, yet another interesting tricyclic system should be considered, the phenalenyl system (CXIII), which is remarkable in that it can exist in the form of the comparatively stable cation (CXIV), the anion (CXV), and the free radical (CXVI):



The phenalenyl cation (CXIV) was obtained by Pettit[267] by a method developed previously for the synthesis of tropylium salts. The action of diazoacetic ester on acenaphthylene yielded an acid, which was then converted, after a Curtius rearrangement, into a covalent isocyanate and then into a covalent chloride. The latter was converted into phenalenylium perchlorate on treatment with silver perchlorate:

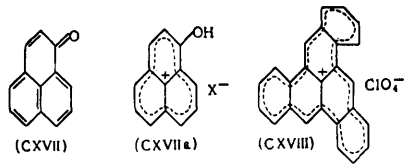


This salt is insoluble in non-polar solvents and soluble in strong acids, but it is readily hydrolysed and is not stable in air. The same salt can be obtained by interaction of silver perchlorate with the phenalenyl radical[268]:

$$C_{13}H_9^{\cdot} + AgClO_4 \rightarrow C_{13}H_9^{+}\,ClO_4^{-} + Ag.$$

The properties of phenalenylium iodide $C_{13}H_9I$ also indicate the ionic character of the link between the iodine and the organic residue[268].

The phenalenylium cation, although less stable than the tropylium cation, is, however, far more stable than the triphenylmethyl cation. The ability of the phenalenyl system to form a cation is shown also in the properties of the corresponding ketone, phenalenone (CXVII), which in many respects resembles tropone. Thus, phenalenone is soluble in acids and yields comparatively stable salts of the type (CXVIIa)[269, 270].

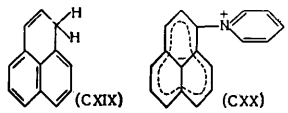


A close analogy with tropone is indicated also by the comparatively high dipole moment of phenalenone, which according to Zhdanov et al.[271] is 3.99 D (in dioxan). The complex formed by the ketone with $SbCl_5$ has a still higher dipole moment (8.49 D).[271] The ultra-violet spectrum of phenalenone perchlorate is very similar to that of the perchlorate of the phenalenyl cation[272]. The lower frequency of the CO bond in the ketone (1637 cm^{-1}) also points to considerable polarisation of the carbonyl group. The tribenzophenalenyl cation (CXVIII) also possesses similar stability. and also gives a quite stable perchlorate[273].

On the other hand, the properties of the original hydrocarbon, phenalene (CXIX), indicate that, like cyclopentadiene, indene, and fluorene, it is readily converted into the corresponding anion (CXV) by strong bases (phenyllithium, potassium methoxide)[272]:

$$C_{13}H_{10} + CH_3O^- \rightarrow C_{13}H_9^- + CH_3OH.$$

This anion is coloured an intense red; on treatment with methyl iodide it is alkylated forming methylphenalene. The ready formation of an anion is shown also by the fact that, like cyclopentadiene, phenalene readily condenses with benzaldehyde in the presence of bases. The hydrogen of the methylene group of phenalene is considerably more acidic than that in triphenylmethane, although less so than that in cyclopentadiene. Phenalene may be expected, like cyclopentadiene, to form stable "ylides" of the type (CXX).



The stable phenalenyl radical (CXVI) is also formed unusually readily[268,272,274]. Thus the phenalenide anion (obtained from phenalene by the action of potassium methoxide) on shaking in air is oxidised by molecular oxygen to the free radical:

$$C_{13}H_{10} \xrightarrow{OR^-} (C_{13}H_9:)^- \xrightarrow{+O_2} C_{13}H_9^{\cdot} + O_2 .$$

Phenalene reacts with triphenylmethyl to form triphenylmethane and the phenalenyl radical[272]:

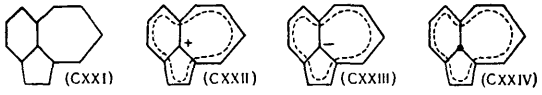
$$C_{13}H_{10} + (C_6H_5)_3C^{\cdot} \rightarrow C_{13}H_9^{\cdot} + (C_6H_5)_3CH.$$

Finally, phenalenyl is formed by treating phenalene with *N*-bromosuccinimide, by the action of organic bases on phenalene 2,3-dibromide[272], and also by the oxidation of phenalene with osmium tetroxide in the presence of pyridine[268]. This free radical can be isolated in the solid form. It has a green colour, does not react with nitric oxide, and adds on oxygen forming a peroxide.

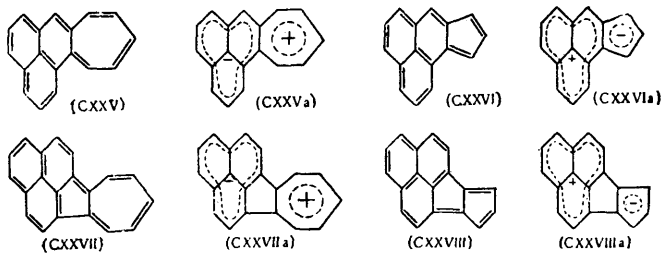
Apart from the unsubstituted phenalenyl radical, the following derivatives have now been obtained as stable radicals: 1,4,7-trimethyl, 1-hydroxy-3-phenyl, 1-methoxy, 1-acetoxy, and 1-benzoyloxy derivatives[275].

Thus the phenalenyl system can form a stable cation, anion, and free radical, which are appreciably more stable than the corresponding triphenylmethyl forms. This feature of the system can be explained by the character of its molecular orbitals. Calculation[23] shows the phenalenyl system to have molecular orbitals with the following energy values (in β units): six bonding (-2.45, -1.73, -1.73, -1.00, -1.00, and -1.00), one non-bonding (0), and six anti-bonding orbitals. The twelve π electrons of the cation can be arranged in six bonding orbitals, which explains its stability. On the other hand, the non-bonding orbitals can take up, without any gain or loss in energy, either one or two electrons with the formation of a radical or an anion respectively. The energy of the cation, radical, and anion proves to be the same (15.82 β). Thus, although the phenalenyl system does not possess a closed electron shell, it will be stable, depending on the conditions, in strongly acid media in the form of a cation, in strongly alkaline media in the form of an anion, and in the presence of free-radical reagents or when acted upon by oxidising agents in alkaline media or reducing agents in acid media in the form of a free radical. The triphenylmethyl system, which possesses analogous properties (although less strongly marked), also has one non-bonding level of zero energy.

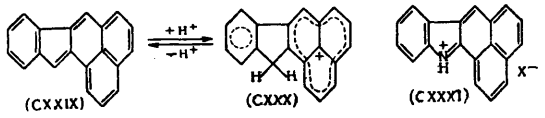
There is every reason to suppose that other cyclic systems containing an odd number of atoms and possessing non-bonding orbitals should also exhibit their own kind of "amphoteric" properties, like the phenalenyl system. Thus, for example, the system (CXXI), which is isoelectronic with the phenalenyl system and has six bonding, one non-bonding, and six anti-bonding orbitals[23], should apparently form the stable cation (CXXII), anion (CXXIII), and free radical (CXXIV).



On the basis of the "amphoteric" properties of the phenalenyl system described above, Reid[268] suggested that it will be able to form dipolar compounds of the azulene type, in which either the five-membered or the seven-membered ring may be replaced. Such are the aromatic systems (CXXV)–(CXXVIII), which like azulene should show a tendency to be polarised to (CXXVa)–(CXXVIIIa).



Reid was able to obtain a benzo derivative of one of these systems, indeno[2,1-*a*]phenalene (CXXIX)[274]:



This hydrocarbon, like azulene, possesses basic properties and dissolves in strong acids forming the corresponding cation (CXXX) (green colour). The basic strength of (CXXIX) is equal to that of azulene. It readily undergoes electrophilic substitution, being acetylated (even in the absence of catalysts) and nitrated. Reid also obtained heterocyclic nitrogen-containing analogues (CXXXI) of this dipolar system.

However, it was not possible to synthesise the unsubstituted cyclopenta[*a*]phenalene (CXXVI) by dehydrogenation of the corresponding tetrahydro derivative (either catalytically or with sulphur), or by bromination and dehydrobromination.

MACROCYCLIC AROMATIC SYSTEMS

It is theoretically possible on the basis of Hückel's rule that aromatic systems containing not only six but also a large number of π electrons can exist. Aromaticity could apparently be expected in conjugated cyclic polyolefins C_mH_m having m = 10, 14, 18, 22, etc. (corresponding to values of n = 2, 3, 4, 5, etc. in the Hückel formula $4n + 2$).

However, the existence of such macrocyclic systems in the form of plane regular polygons is unlikely owing to the great angular strain, and the transition of the molecules into a non-planar form would considerably diminish the conjugation energy.

A second possibility consists in the formation of a hydrocarbon skeleton of unstrained plane equilateral polygons having internal angles not only of 120° but also of 240°. It is easy to show from general geometrical considerations that, if the number of 120° angles is denoted by x, and that of 240° angles by y, any polygons having both 120° and 240° angles and a total of $2k$ angles (where k is an integer ≥ 3) will conform to the relationship $x = k + 3$ and $y = k - 3$*. The Table gives numerical values of x and y calculated from these relationships for cyclopolyolefins.

Numbers of 120° angles (x) and 240° angles (y) in unstrained plane cyclopolyolefins.

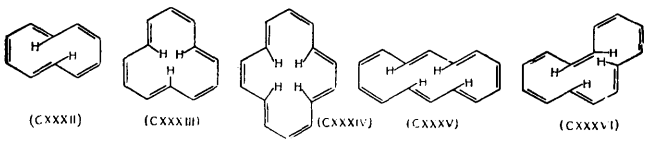
k	$C_{2k}H_{2k}$	x	y
3	C_6H_6*	6	0
4	C_8H_8	7	1
5	$C_{10}H_{10}$	8	2
6	$C_{12}H_{12}$	9	3
7	$C_{14}H_{14}$	10	4
8	$C_{16}H_{16}$	11	5
9	$C_{18}H_{18}$	12	6
15	$C_{30}H_{30}$	18	12

* Only a regular hexagonal structure is possible.

The values of x and y given correspond formally to the unstrained systems cyclodecapentaene (CXXXII) (x = 8, y = 2), cyclododecahexaene (CXXXIII) (x = 9, y = 3), and

* The total number of angles $2k = x + y$; the sum of all the angles is $120x + 240y = 180 \times 2k - 360°$; values of x and y are deduced from these two equations.

cyclotetradecaheptaene (CXXXIV)–(CXXXVI) ($x = 10$, $y = 4$):



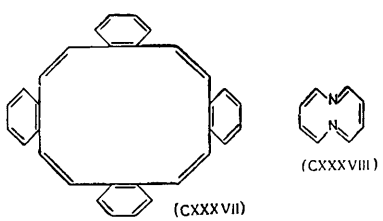
(CXXXII) (CXXXIII) (CXXXIV) (CXXXV) (CXXXVI)

Among these, systems having odd values of k ($C_{10}H_{10}$, $C_{14}H_{14}$, $C_{18}H_{18}$, etc.) should be aromatic according to the Hückel rule. As Mislow[276] showed in 1952, however, if the C–C distance is taken as 1.40 Å, C–H as 1.10 Å, and the van der Waals radius of hydrogen as 1.10 Å, a very marked repulsion between the central hydrogen atoms is to be expected in all such molecules. This repulsion would produce a considerable distortion of the system and force it out of planarity. It is only when the ring has grown considerably, to $C_{30}H_{30}$, that the interaction between the central hydrogen atoms can be neglected. Mislow pointed out that the conjugation energy calculated for cyclotriacontapentadecaene, $C_{30}H_{30}$, is 140 kcal/mole, and the compound may be expected to be aromatic.

Until recently no experimental results were available on the properties of macrocyclic polyenes of this type. The hydrocarbon $C_{10}H_{10}$, obtained by Reppe together with cyclooctatetraene in the polymerisation of acetylene[277], proved to be not cyclodecapentaene, as was supposed at first, but a mixture of vinylcyclooctatetraene and 1-phenylbuta-*cis*-1,3-diene[278,279]. The hydrocarbon $C_{12}H_{12}$, formed under the same conditions, is evidently not cyclododecahexaene, although there is as yet no reliable information on its structure.

In the dehydrogenation of various cycloalkanes on palladised charcoal Prelog et al.[280] failed to obtain monocyclic polyenes. Intracyclic formation of new carbon–carbon bonds with the production of polycyclic structures always occurred. Thus cyclodecane changed into azulene and naphthalene, cyclododecane into acenaphthene and acenaphthylene, cyclotetradecane into phenanthrene and anthracene, and cyclohexadecane into fluoranthene. However, the small amounts of the initial cycloalkanes (1–2 g) and the low yields of dehydrogenation products (20–30%) in Prelog's experiments make it possible to ascertain only the main direction of the reaction, and do not exclude the possibility of the formation of comparatively small quantities of cyclopolyenes. Further, as a result of the high temperature (400°), any cyclopolyenes which are formed may undergo secondary conversion into polycyclic systems. This question obviously requires further experimental investigation.

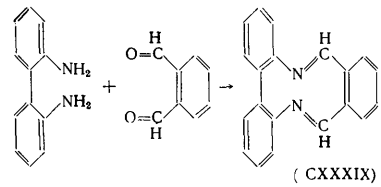
Few data exist on the tetrabenzo derivative of cyclohexadecaoctaene (CXXXVII), which is non-planar and contains olefinic double bonds in the *trans*-configuration according to its infra-red spectrum[281]; this ring with sixteen π electrons could not be expected to be aromatic in character according to the Huckel rule:



(CXXXVII)

(CXXXVIII)

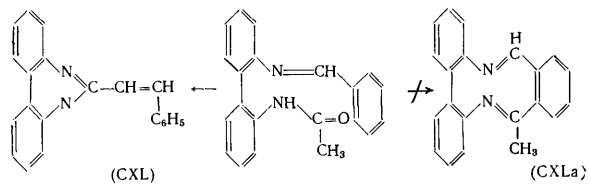
Recently several new approaches to the synthesis of aromatic macrocycles have been proposed. Blood and Noller[282] suggested that the repulsion between the central hydrogen atoms in the cyclodecapentaene system could be avoided by replacing the appropriate CH groups by N. They considered that the nitrogen analogue, 1,6-diazacyclodecapentaene (CXXXVIII) should (1) be unstrained, (2) be planar, (3) have no central H atoms, and (4) possess ten π electrons and be aromatic in conformity with the Hückel rule. However, no success was obtained in an attempt to synthesise the tribenzo derivative (CXXXIX) of such a system by the reaction



(CXXXIX)

only products of high molecular weight were formed. Evidently only linear polycondensation occurs in the course of the reaction.

Moreover, this system could not be obtained by intramolecular cyclisation of *N*-benzylidene-*N'*-acetyl-2,2'-diaminobiphenyl, the seven-membered ring closing (CXL), but not the ten-membered ring (CXLa):

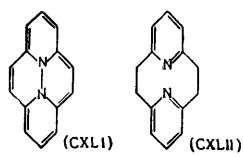


(CXL) (CXLa)

The reason for the failure of this work is obviously the omission by the authors from their theoretical premises of the considerable repulsion between the neighbouring nitrogen atoms in the 1,6-diazacyclodecapentaene system, although the distance between them (~ 1.4 Å) is only half the sum of the van der Waals radii of the two nitrogen atoms (~ 3 Å).

Nevertheless, this idea of Blood and Noller's must be regarded as useful, but it can be applied only to larger rings, in which the distances between the central atoms are considerably greater.

Another similar approach to the formation of macrocyclic aromatic systems was suggested by Baker[283]. Thus, for example, the system (CXLI) in Baker's opinion possesses the peripheral conjugated cyclotetradecaheptaene system with fourteen π electrons. This system should be almost unstrained, though it is possible that one nitrogen atom is above the plane and the other beneath it. So far Baker et al. have described only the tetrahydro derivative (CXLII), and there is some indication that its dehydrogenation leads to (CXLI)[283]:

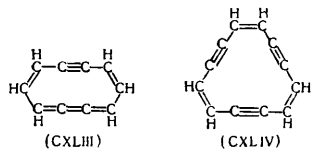


(CXLI) (CXLII)

However, one substantial defect is inherent in this interesting approach to the stabilisation of macrocyclic polyenes: there are no grounds for assuming that the lone pairs of p electrons of the nitrogen atoms will be isolated from the π electrons of the aromatic system. It is highly probable

that these p electrons will form a new system, different from the cyclotetradecaheptaene system and with different energies of the ground and excited states, in which the nitrogen bridge will form part not only of the framework but also of the aromatic system.

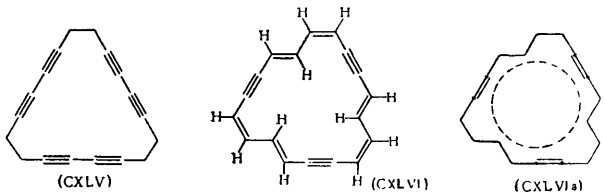
Yet another path to aromatic macrocycles, suggested by Sworski[284], consists in introducing linear acetylenic or cumulene groups into the benzene ring. Such are the systems (CXLIII) and (CXLIV), which can be written in the form of Kekulé structures having unstrained angles and are planar; every carbon atom in them has a p-orbital perpendicular to the ring:



(CXLIII) (CXLIV)

Sworski concludes that both these systems should be aromatic. The first contains fourteen π electrons, of which ten form a conjugated system, so that it obeys the Hückel rule. In the second, however, only twelve of the eighteen π electrons can take part in the conjugation, so that according to this rule the system should not be aromatic.

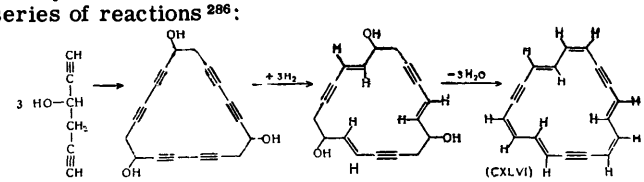
Sondheimer and Wolovsky[285] in 1959 published a paper on the synthesis of the first such macrocycle containing, in conformity with Sworski's hypothesis, triple bonds. Oxidation of hexa-1,5-diyne with copper acetate in pyridine yields the trimer, cyclooctadeca-1,3,7,9,13,15-hexayne (CXLV). This on treatment with potassium t-butoxide in t-butyl alcohol (at 90°) undergoes rearrangement to a substance which has been given the structure cyclooctadeca-*cis*-1,7,13:*trans*-3,9,15-hexaene-5,11,17-triyne (CXLVI). As can be seen from the structural formula, the ring in (CXLVI) has the form of a plane polygon, the distance between the internal hydrogen atoms being sufficiently great for their mutual repulsion to be low. This molecule contains twenty-four π electrons, of which eighteen form a conjugated system obeying the Hückel rule ($4n + 2$ with $n = 4$). A closed electron shell is thus formed, and this system is aromatic (cf. CXLVIa).



(CXLV) (CXLVI) (CXLVIa)

Too few results are yet available to confirm whether the substance obtained by Sondheimer and Wolovsky actually has the structure indicated. In their opinion this is supported by the ease of formation of the compound, its comparative stability (it decomposes only at 200°, and is stable to the action of light and air), and, confirming a monocyclic structure, its catalytic hydrogenation to cyclooctadecane.

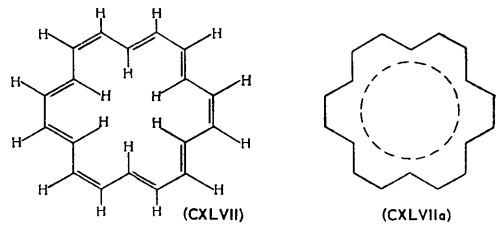
In order to prove the structure (CXLVI), the compound was synthesised from hexa-1,5-diyn-3-ol by the following series of reactions[286]:



It cannot be agreed, however, that this synthetic path proves the structure (CXLVI), since it was not possible to isolate any of the intermediate compounds in a pure form or to identify them.

This macrocyclic aromatic compound is of such great theoretical interest that a more rigorous determination of its structure will undoubtedly be made shortly. If the structure (CXLVI) is confirmed, it will be the first monocyclic aromatic compound to contain more than six π electrons. It will be interesting also as the first stable aromatic compound containing triple bonds in the ring, thus being an analogue of dehydrobenzene, whose transient formation has been established in a number of cases[287].

Especially interesting results were obtained by Sondheimer and Wolovsky[288] by the selective hydrogenation of (CXLVI) on a palladium catalyst, when *trans* addition of six hydrogen atoms to the triple bonds occurred with formation of cyclooctadecanonaene (CXLVII):



(CXLVII) (CXLVIIa)

This hydrocarbon contains a conjugated system of eighteen π electrons and thus conforms to the Hückel rule; its molecule can be planar or almost planar and relatively unstrained. Consequently, according to the criteria of aromaticity discussed above, cyclooctadecanonaene should exhibit aromatic properties. It was actually found to have a centrosymmetric, almost planar structure and to be considerably more stable than its acyclic analogue $CH_3.[CH:CH]_9.CH_3$. It is stable on heating even to 230°, although it gradually decomposes on prolonged standing in the light and in air. This substance is the first macrocyclic aromatic compound known, and can be represented by formula (CXLVIIa). It must be assumed that non-benzenoid aromatic macrocycles of this type will be the object of intense research in the immediate future.

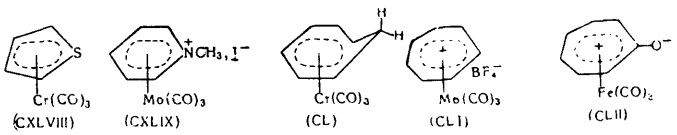
AROMATIC COMPLEXES OF METALS

During the past seven or eight years a completely new field of organic chemistry, the chemistry of aromatic complexes of metals, has arisen and has been vigorously developed.

The detailed reviews by Nesmeyanov and Perevalova on the cyclopentadienyl derivatives of metals and related systems[289] and by Dyatkina on the structure and nature of the bonds in these compounds[290] make it unnecessary to dwell on this question.

Recently the range of aromatic and unsaturated systems which form complexes with transition metals has been considerably extended. Among complexes which have been obtained are tricarbonylthiophenchromium (CXLVIII)[291], dicarbonylthiopheniron[292,293], tricarbonyl-1-methylpyridiniummolybdenum iodide (CXLIX)[292,293], tricarbonylcycloheptatrienechromium (and -molybdenum) (CL)[294], and finally

tricarbonyltropyliummolybdenum fluoroborate (CLI) and tricarbonyltroponeiron (CLII)[295,296]:



(CXLVIII) (CXLIX) (CL) (CLI) (CLII)

Diamagnetic complexes of cycloheptatriene and tropylium with salts of platinum, $(C_7H_8PtBr_2)_2$ and $(C_7H_7PtBr_2)_2$,[297] have also been obtained, as well as complexes of carbonyls of the transition metals with azulene, $C_{10}H_8Fe_2(CO)_5$ [292,293] and $C_{10}H_8Mo_2(CO)_6$,[298] in which one azulene molecule is associated with two atoms of the metal.

These results suggest that all aromatic systems are able through their π electrons, to form compounds with transition metals (or their carbonyls). This property, however, is characteristic not only of aromatic rings. Thus we have the complexes formed by cyclobutadiene with $AgNO_3$ and by tetramethylbutadiene with $NiCl_2$ which have already been considered, as well as cycloheptatriene complexes. An analogous complex of cyclooctatetraene has recently been obtained[299,300]. Complexes with carbonyls are formed even by bicycloheptadiene, whose system of multiple bonds is not conjugated[292,301].

The important question still remains open as to whether the cyclobutadiene and cyclooctatetraene systems become aromatic after they have formed complexes with transition metals. Interaction of the ring with the metal produces a new system of molecular orbitals, and there is every ground for supposing that the electron system in such complexes will be closed and stable in spite of the π-electron system in the original hydrocarbons being "unclosed".

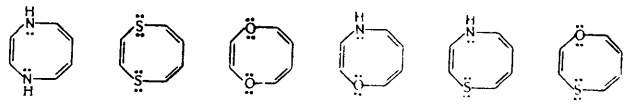
AROMATIC HETEROCYCLES

A large number of five- and six-membered heterocycles possessing an aromatic sextet of π electrons are now known. Owing to lack of space, only certain general aspects of aromatic heterocyclic systems will be considered here.

As Baker[2] points out, any systems of these types can be derived by replacing one or several =CH– groups in the Kekulé formula for benzene by =N– (e.g. pyridine), $=\overset{+}{N}R-$ (pyridinium derivatives), $=\overset{+}{O}-$ (pyrylium salts); or a –CH: :CH– group by hetero atoms having a lone pair of p electrons: –NH– (pyrrole), –NR– (N-substituted pyrroles), –O– (furan), –S– (thiophen). The "perturbation" caused by introduction of hetero atoms is not very great, and has no effect on whether or not the electron shell of the molecule is closed[20].

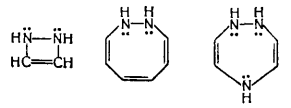
Baker establishes the following limitations to the formation of aromatic heterocycles: (1) for the heterocycle to retain its aromatic character it should be a five-, six-, or seven-membered ring; (2) formation of the heterocycle may be impeded by certain chemical restrictions, e.g. the instability of the –O–O– link.

The first of Baker's limitations is hardly correct. There are no grounds for supposing that eight-membered heterocycles should, like cyclooctatetraene, completely lose their aromatic character. Moreover, aromaticity can evidently be expected in the hypothetical eight-membered systems



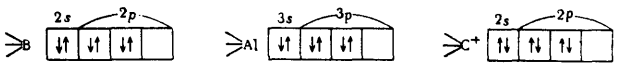
They form a closed system of ten π electrons, and thus conform to Hückel's rule (although they may not be completely planar). Just as five-membered heterocycles are "element-homologues" of the cyclopentadienyl anion, the eight-membered rings may be regarded as analogues of the $C_8H_8^{2-}$ anion. Synthesis of systems of this type could be of great theoretical interest.

On the other hand, a further restriction must be placed on the "construction" of heterocyclic aromatic systems. A single conjugated system of π electrons cannot be formed if a –CH : CH– group is replaced by two neighbouring hetero atoms; i.e. if the heterocycle contains side by side two atoms which are donors of p electrons and are linked by single bonds*. For example, aromaticity cannot be expected in the following heterocyclic systems, in spite of the presence in them of six or ten π electrons:

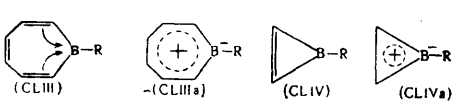


Besides the two methods of formation of aromatic heterocycles formulated by Baker (replacement of –CH= and –CH : CH– groups), there is another possibility which he did not consider: heterocyclic systems which are analogues of tropylium can be formed from the benzene system by addition of a hetero atom with a free orbital.

Whereas the characteristic aromatic heterocyclic analogues of the cyclopentadienyl anion are five-membered rings containing hetero atoms possessing a lone pair of electrons, the tropylium system may be expected to have seven-membered analogues containing hetero atoms possessing a vacant p-orbital, primarily boron and aluminium:



The electronic configuration of tervalent boron very closely resembles that of the carbon atom. Replacement of one C atom in the tropylium ion by a boron atom should lead to an uncharged molecule which is a seven-membered heterocyclic system having aromatic properties. Thus, the hitherto unknown 7-boratropylidene ("borepin") (CLIII) may be expected to form a stable aromatic system having six π electrons:



(CLIII) (CLIIIa) (CLIV) (CLIVa)

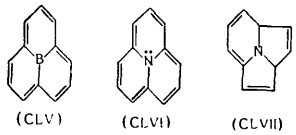
* This is because the number of bonding molecular orbitals is insufficient to contain all the p electrons in such cases.

As a result of the filling of the vacant orbital of the boron atom, the latter should become to a considerable extent quadricovalent and negatively charged, and the carbon atoms should acquire some positive charge: the molecule as a whole should possess an appreciable dipole moment (see CLIIIa).

Similar arguments lead to the conclusion that the existence of a three-membered aromatic system containing boron as hetero atom (CLIV or CLIVa) is possible.

This qualitative picture and the prediction of the existence of the new aromatic system borepin[73] have recently been supported by quantum-mechanical calculations made by Bochvar et al.[302]. It was found that the "perturbation" produced by replacing a $-CH=$ group by a less electronegative hetero atom does not affect the closed character of the electron shell, and borepin like tropylium should possess three bonding and four non-bonding orbitals with six π electrons; i.e. it should be aromatic.

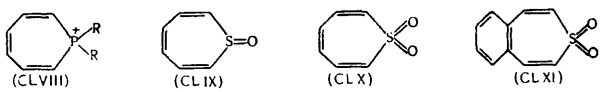
Interesting heterocyclic analogues may be suggested also for the phenalenyl system, which, as has been seen, exists both as a stable cation and as a stable anion (CXIV and CXV). When the central C^+ atom in the cation is replaced by the isoelectronic boron atom[268], and the C^- atom in the anion by the isoelectronic nitrogen atom, the uncharged systems (CLV) and (CLVI) are obtained, and these should evidently possess aromatic stability (although their peripheral hydrocarbon system possesses twelve π electrons).



(CLV) (CLVI) (CLVII)

The name "cyclazines" has recently been suggested for nitrogen-containing compounds of this type, and the first representative of these heterocycles, cycl[3,2,2]azine (CLVII), has been synthesised[303]. This compound, in contrast to pyrrolidine, does not possess basic properties. This means that the lone pair of electrons of the nitrogen atom takes part in the formation of an aromatic system, which is isoelectronic with the hypothetical anion (CXV) considered above. Cycl[3,2,2]azine is extremely stable and readily undergoes aromatic electrophilic substitution.

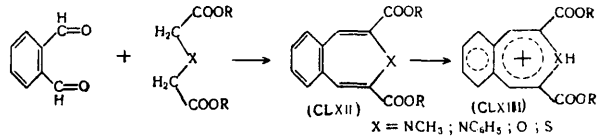
It may be expected that elements not only of Group III but also of other groups of the Periodic System which have vacant *p* or *d* orbitals (e.g. quadricovalent phosphorus) will be able to form aromatic systems analogous to those considered above, e.g. (CLVIII)–(CLXI):



(CLVIII) (CLIX) (CLX) (CLXI)

The arguments of Truce and Lotspeich[304] in support of the absence of aromatic properties in benzo-3-thiepin 3-dioxide (CLXI) are not convincing, since they did not investigate the behaviour of this compound towards acids, and it is in acid solutions that, like tropone, it should exhibit aromatic stability. Further, the fact that this sulphone is nitrated by concentrated nitric acid[304] may be regarded as a direct indication both of its aromatic character and of its stability towards acids.

It is interesting that Dimroth et al.[305-307] have found that derivatives of 7-aza-, 7-oxa-, and 7-thiabenzotropylidene (CLXII) in acid solution form stable salts of the type (CLXIII), which are heterocyclic analogues of the benzotropylium cation:



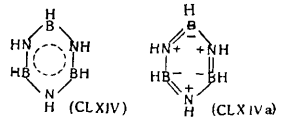
(CLXII) (CLXIII)

X = NCH_3 ; NC_6H_5 ; O ; S

INORGANIC AROMATIC COMPOUNDS

Successive replacement of all the carbon atoms in benzene or other aromatic systems by appropriate hetero atoms will yield compounds containing no carbon but retaining their aromatic properties.

The first example of this type was borazole ("inorganic benzene") (CLXIV), obtained by Stock and Pohland[308] in 1926 and now well investigated. In the six-membered borazole ring the boron atoms contain vacant *p*-orbitals, and the nitrogen atoms unshared pairs of *p*-electrons:



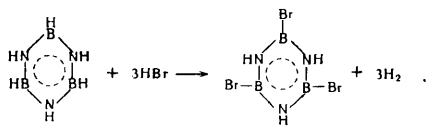
(CLXIV) (CLXIVa)

Conditions are thus created for the formation of molecular orbitals of the same type as in benzene, in which six π electrons are distributed. As a result, the boron atom becomes quadricovalent and negatively charged, while the nitrogen atom becomes quadricovalent and positively charged (cf. the "Kekulé" structure CLXIVa). The aromaticity to be expected in such a system is confirmed by electron diffraction data[309,310], according to which the borazole molecule is a planar equilateral hexagon with D_{3h} symmetry and NBN and BNB angles of 120°. The B–N interatomic distances are 1.44 Å, very close to the C–C bond lengths in benzene (1.42 Å); the experimental value lies between those calculated for single B–N bonds (1.50 Å) and for double B=N bonds (1.35 Å). Similar results were obtained for substituted borazoles[311].

Among the chemical properties of borazole its high thermal stability is remarkable. Thus it remains completely undecomposed even after being heated at 500° for 12 h.

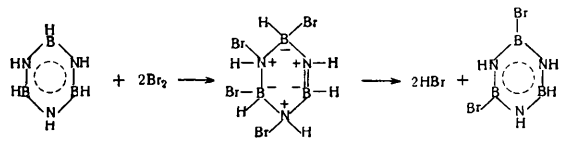
Borazole proves to be less stable than benzene towards chemical reagents (see Wiberg's review[312]). Even at room temperature it adds on hydrogen halides, water, alcohols, bromine, and chlorine, excess of the reagents frequently disrupting the borazole ring.

However, it is possible by heating with HBr at 100° or with HCl at 450° to replace hydrogen by halogen with the formation of substituted borazoles[313,314]:



This reaction is analogous to nucleophilic substitution in benzene derivatives.

Substitution products are formed also by the action of elementary bromine on borazole, this reaction occurring via intermediate addition of bromine and thermal decomposition of the adduct (slowly at room temperature, rapidly at 60°–70°)[313]:



All these results confirm the aromatic character of the borazole system.

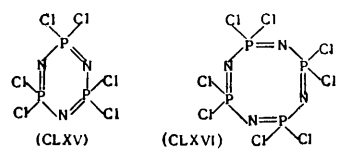
A further interesting class of inorganic aromatic compounds is formed by the cyclic phosphoronitrile halides $(PNX_2)_n$.[315]

The most accessible of them, the chlorides, can be readily synthesised by heating phosphorus pentachloride with ammonium chloride[316,317]:

$$n\,PCl_5 + n\,NH_4Cl \rightarrow (PNCl_2)_n + 4n\,HCl.$$

Phosphoronitrile chlorides are obtained with n = 2, 3, 4, 5, 6, and 7;[318] a linear polymer $(N:PCl_2)_n$ is also known.

The most thoroughly studied of these compounds are the trimer $P_3N_3Cl_6$ and the tetramer $P_4N_4Cl_8$, for which a monocyclic structure has been firmly established. By analogy with organic compounds, the formulae (CLXV) and (CLXVI), with alternating single and double bonds, can be written for the trimer and the tetramer:



(CLXV) (CLXVI)

Brockway and Bright[319] have shown by means of electron diffraction that the six-membered ring of the trimer is planar: all the PN bonds are equal with the chlorine atoms linked to phosphorus and situated below and above the ring. The interatomic PN distances are 1.65 Å; i.e. they lie between the values calculated for single and double bonds between phosphorus and nitrogen (P–N 1.80, P=N 1.61 Å). The PCl distances are 1.97 Å (calculated for P–Cl 2.09, for P=Cl 1.89 Å). The Cl–P–Cl angles are 107°–110°, and the N–P–N and P–N–P angles are 120°.

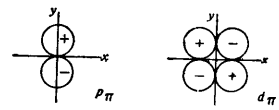
X-ray data show that, although the eight-membered ring of the tetramer is not planar, all the P–N distances are the same[320], like those in the six-membered ring. This result appears at first sight unexpected in view of the non-equivalence of the carbon–carbon bonds in the corresponding organic analogue, cyclooctatetraene.

The reactivities of the six- and eight-membered cyclic phosphoronitrile chlorides also proved to be similar. They are characterised by the comparative stability of the cyclic part of the molecule and the ready substitution of the chlorine atoms by other groups (OH, NR_2, C_6H_5) by the action of nucleophilic reagents such as water, amines, and phenylmagnesium bromide[321–325]. The chlorine atoms can be readily replaced by the phenyl group by condensation with benzene in the presence of aluminium chloride[326].

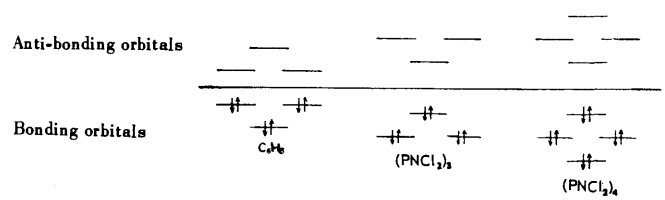
Particularly interesting results have been obtained in a quantum-mechanical examination of the cyclic phosphoronitrile chlorides carried out by Craig and Paddock[327–329].

Formation of the aromatic systems of benzene and other organic compounds involves the p-orbitals of the carbon atoms (p_π orbitals), and as a result of their interaction common molecular orbitals are produced. In the phosphoronitrile chlorides the nitrogen, like the carbon in benzene, can use its p_π orbital for the formation of an aromatic bond. The phosphorus atom, however, already linked to four other atoms by single bonds formed by one s and three p orbitals (sp^3 hybridisation), has only the nearest d_π orbital unoccupied. Thus the molecular orbitals in the cyclic phosphoronitrile chlorides are formed from alternating p_π and d_π atomic orbitals.

The six-membered ring of the trimer $(PNCl_2)_3$, like that of benzene, has three bonding molecular orbitals, among which are distributed six π electrons. However, as a result of p_π–d_π interaction, these molecular orbitals differ appreciably from those in benzene, the essential point being that the d_π orbitals have a different symmetry of the electron cloud from the p_π orbitals, as well as different energy levels:



This difference is shown in the phosphoronitrile chlorides by an exchange of positions between the degenerate and the non-degenerate level (see scheme below). Besides this, the highest bonding level now lies somewhat above that in benzene and is closer to the lowest non-bonding level, resulting in a lower excitation energy of the molecule.



The effect of the symmetry of the d orbitals of phosphorus becomes still more evident on passing from the six-membered trimer to the eight-membered ring of the tetramer. A new bonding orbital appears, in which two new π electrons are distributed. Thus, in contrast to cyclooctatetraene, a closed electron shell is formed in the eight-membered phosphoronitrile chloride, and the latter molecule should exhibit aromatic stability. The aromatic character of the tetramer is confirmed by the equality between the interatomic distances in the ring, and also by its chemical properties.

A similar result is obtained by the application of quantum-mechanics to rings containing ten, twelve, etc. atoms. The Hückel rule of $(4n + 2)$ π electrons in aromatic systems is confined solely to p-orbital interaction. In the case of p_π–d_π interactions, however, a closed system is formed with any even number of π electrons (formula $2n$ where n is an integer).

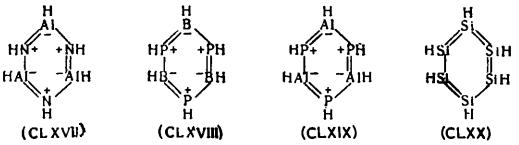
Craig and Paddock[327] have calculated the following energy values for a single π electron in cyclic phosphoronitrile chlorides (in appropriate δ units) and in cyclic hydrocarbons (in β units) (for plane systems):

Compound	Number of electrons (n)				
	4	6	8	10	12
C_nH_n	1.0	1.33	1.20	1.30	1.243
$(PNCl_2)_{n/2}$	1.78	1.87	1.89	1.90	1.908

The Table shows that, whereas in the hydrocarbons there is an alternation in stability, in the phosphoronitrile halides the energy increases steadily up to n = 8–10, and then remains constant. It is possible, however, that the absence of planarity in the higher rings will cause a diminution in the stability of the molecules.

The quantum-mechanical examination of the phosphoronitrile halides as an aromatic system provides yet another way of applying to inorganic compounds the laws and concepts of organic chemistry. These compounds may be supposed to form the first but by no means the only example of p_π–d_π aromatic systems.

Similarly, a number of new inorganic systems having p_π interaction may be expected to possess an aromatic character. Thus Wiberg[312] suggests the possibility of the existence of such "element homologues" of borazole as "alazole" $Al_3N_3H_6$ (CLXVII), "boraphosphole" $B_3P_3H_6$ (CLXVIII), and "aluphosphole" $Al_3P_3H_6$ (CLXIX), in which, as in borazole, atoms having vacant p orbitals alternate with atoms possessing free pairs of p electrons.



(CLXVII) (CLXVIII) (CLXIX) (CLXX)

Of interest in this connection is the preparation of a silicon analogue of benzene described by Urry[330]:

$$SiCl_4 \xrightarrow{Si} Si_6Cl_6 \xrightarrow{LiBH_4} Si_6H_6.$$

The reaction of the hexachloro derivative Si_6Cl_6 with dimethylmercury also yields a hexamethyl derivative $Si_6(CH_3)_6$. These compounds are apparently the first homocyclic analogues of benzene.

The chemistry of inorganic aromatic compounds has only just begun to develop, but it is clear from the examples already given that the concept of aromaticity can be successfully applied also to inorganic substances.

CONCLUSION

The concept of aromaticity arose nearly a hundred years ago as a purely qualitative idea without any physical basis. Since that time the range of aromatic systems has considerably expanded and has embraced compounds of the most varied classes. The quantum-mechanical approach to the structure of organic compounds has enabled a great stride forward to be made in the development of the chemistry of aromatic compounds. A particularly important part in this has been played by the molecular-orbital method, by means of which fundamental criteria of aromaticity have been formulated.

Progress in theoretical and synthetic organic chemistry in this field now enables us to determine afresh and more rigorously what compounds should be regarded as aromatic.

Baker[1], in 1945, wrote in his review on non-benzenoid aromatic compounds that " a molecule may be said to be of aromatic type if it is a cyclic unsaturated compound containing at least two conjugated double bonds in the ring, when represented by the conventional symbols, and in which these bonds interact to a greater or lesser extent [with one another]..."

It follows from the above account that this definition cannot now be regarded as in any way satisfactory. On the one hand aromatic compounds with a single pair of π electrons (one formally "double" bond) — cyclopropenylium derivatives — are known; on the other hand, such compounds as cyclobutadiene, pentalene, and heptalene, and many others are not aromatic, in spite of the formal presence of conjugated double bonds and of interaction between them.

A more rigorous definition, which in recent times has been widely quoted in a number of papers, was given in 1949 by Dewar[331], who regarded as aromatic those cyclic compounds having a large conjugation energy, and in which all the atoms in the ring take part in the formation of a single conjugated system.

It can be shown, however, that this definition, too, is inadequate. Thus, for example, in the cycloheptatrienyl anion all the ring atoms take part in the formation of a single conjugated system, and calculations show the anion to possess a considerable conjugation energy (2.83 β), but it occurs in a diradical ground state and is not aromatic. Nor are pentalene and heptalene aromatic, in spite of their considerable conjugation energies (2.49 and 3.61 β). Thus even Dewar's definition cannot be regarded as correct: it includes all the necessary, but not the sufficient, conditions for aromaticity, since no account is taken of the closed character of the electron shell in aromatic systems.

In conformity with the above remarks, the following definition of aromatic compounds may be given: *aromatic compounds are those unsaturated cyclic compounds in which all the ring atoms take part in the formation of a single conjugated system, and the π electrons of this system form a closed electron shell.*

By a "closed electron shell" is understood a system of π electrons such that both removal of electrons from it, and addition of further electrons to it, increase the total energy of the system, and consequently diminish its stability. In terms of the molecular-orbital method this means that all the π electrons occur only in bonding molecular orbitals, to each of which are allocated two electrons.

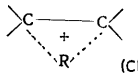
The formation of a closed electron shell determines the fundamental physical and chemical properties common to all aromatic systems: high energetic stability, with comparative ease of formation; predominance of substitution reactions, instead of addition at the multiple bonds; bond order intermediate between single and double bonds; planar or nearly planar structure of the molecule; and equivalence of carbon–carbon bonds in unsubstituted monocyclic carbocycles.

The past decade has been marked by great progress in the synthesis and investigation of non-benzenoid aromatic systems. This new field of organic chemistry is characterised by a mutual exchange of ideas and close collaboration between quantum-mechanical and synthetic methods of research. The fertility of the idea of aromaticity has been clearly demonstrated by the prediction and discovery of tropylium salts, π complexes of metal salts with cyclobutadiene, and new types of inorganic systems.

The concept of the special stability of an aromatic system of six electrons has been successfully applied by Syrkin[332] to the interpretation of the mechanisms of a large number of organic reactions. The activation energy is appreciably reduced when a conjugated system of six electrons is formed in the transition state, and therefore many reactions occur via the formation of five-, six-, and seven-membered transition states, which are in a way electronic analogues of the

cyclopentadienide, benzene, and tropylium aromatic systems.

Similarly, the occurrence of 1,2-migration during many rearrangements may be explained by the ease of formation of a system consisting of two electrons in the field produced by three nuclei. Among such electronic analogues of the cyclopropenylium aromatic system are also the so-called π complexes and "non-classical" ions of the carbonium type (CLXXI).



(CLXXI)

During the next few years a further intense development in the chemistry of non-benzenoid aromatic compounds may be expected, and in particular the synthesis of new aromatic macrocycles, the cyclopropenylium cation, and of new heterocyclic (e.g. containing boron), polycyclic, and inorganic aromatic systems.

On the other hand, the use of non-benzenoid aromatic compounds in organic synthesis provides new ways of preparing various compounds having new, previously unattainable properties, and will undoubtedly lead to valuable practical results.

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ELECTROLYTIC CONDENSATION OF CARBOXYLIC ACIDS

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INTRODUCTION

Investigations on electrolytic condensation processes and, in general, on organic electrosynthesis, were first carried out in 1849 by Kolbe who obtained ethane and carbon dioxide at the anode during the electrolysis of an aqueous solution of potassium acetate (in the hope of separating the methyl radical)[1]. Later it was found that the electrolysis products also contained ethylene and methyl acetate[2].

Kolbe believed that the substances formed at the anode were products of the partial oxidation of acetic acid with oxygen which was liberated at the anode, and therefore found it impossible to evaluate the reaction that he had discovered. Electrolytic condensation methods were used extensively in preparative organic chemistry as early as the second half of the 19th century. The fundamental nature of the Kolbe reaction became clear: a discharge of the carboxylic acid anions with subsequent decarboxylation and "fusion" of the radicals:

$$\left.\begin{matrix}RCOO^-\\RCOO^-\end{matrix}\right\} \xrightarrow{-2e} R{-}R + 2CO_2.$$

In 1855 Würtz[3,4] first extended the use of the Kolbe synthesis by proving that it was possible to condense acids with varying numbers of carbon-atoms (the so-called "crossed" synthesis):

$$\left.\begin{matrix}R_1COO^-\\R_2COO^-\end{matrix}\right\} \xrightarrow{-2e} R_1{-}R_2 + 2CO_2.$$

Brown and Walker[5] found in 1891 that diesters of dicarboxylic acids could be synthesised by the electrolysis of salts of half-esters of aliphatic dicarboxylic acids:

$$2ROOC(CH_2)_n COO^- \xrightarrow{-2e} ROOC(CH_2)_{2n} COOR + 2CO_2.$$

Subsequent detailed investigations on the electrolytic synthesis of diethyl succinate from ethyl malonate[6-8] confirmed that the Brown–Walker reaction was analogous to the electrolysis of salts of acetic acid and of other acids of the aliphatic series.

At present the term "Kolbe synthesis" is understood to imply electrocondensation at the anode not only of fatty acids but also of their various derivatives, such as the half-esters of dibasic acids. In this reaction water is usually used as solvent, but a series of publications quoted below describe the Kolbe synthesis in solvents such as alcohols, acetic acids, etc.

Side reactions usually occur during the formation of the desired compound, especially when the synthesis is carried out in an aqueous medium. This applies especially to the electrolysis of solutions of salts of carboxylic acids, as first shown by Hofer and Moest[9,10], when an alcohol containing one carbon-atom less than the original acid is also formed:

$$\left.\begin{matrix}RCH_2COO^-\\OH^-\end{matrix}\right\} \xrightarrow{-2e} RCH_2OH + CO_2.$$

The formation of alcohol, according to the Hofer–Moest reaction, can become predominant in an alkaline medium and in the presence of certain anions; in this case the hydroxyl group can occupy not only the α-position in relation to the carboxyl group of the initial compound, but also the β- or even the γ-position[11-15]. Frequently, especially at low current densities, saturated[16-18] and unsaturated[11,14,16,19-22] hydrocarbons* have been detected in the reaction products; these contain 2 carbon atoms less than the normal product:

$$2RCH_2CH_2COO^- \xrightarrow{-2e} RCH_2CH_3 + RCH{=}CH_2 + 2CO_2.$$

* The use of this side reaction for the synthesis of muscone from (3-oxocyclopentadecyl-1)-acetic acid[23] is interesting.

It has been shown that esters[2,16,24-26] and also aldehydes[11,24,27] and ketones[14,16] are formed as by-products during the Kolbe synthesis.

Despite these side reactions, the Kolbe condensation is a most convenient method for preparing various organic compounds. Recently numerous studies have been devoted to it and its practical applications. This review covers publications on anodic condensation reactions up to 1958*.

EFFECT OF EXPERIMENTAL CONDITIONS ON THE COURSE OF THE KOLBE SYNTHESIS

The yield of the principal electrocondensation product and the character of the side-reactions in the Kolbe synthesis are mainly determined by the reaction conditions (anodic current density, anode material, temperature, etc.). The effect of these conditions has been evaluated in detail for the electrolysis of aqueous solutions of alkali-metal acetates[8,35-38] and the synthesis of diethyl succinate from the monoester of malonic acid.

It may be assumed that basic principles, established for these cases, apply generally to electrolytic condensation in aqueous media. The following account of the dependence of the electrolytic condensation on the conditions of electrolysis applies only to aqueous solutions.

1) Effect of Anode Material

In the electrolysis of acetates, the highest yields of ethane are obtained by using a smooth platinum or iridium anode[39]; gold, nickel, and platinised platinum give negative results[37,40-42]. Graphite anodes give moderate yields of ethane, and the quantity of ethane formed depends on the fineness of division of the graphite surface[37]. Analogous effects were found on electrolysis of monoethyl malonate[6,43]. Table 1 shows how the yield of ethane (from potassium acetate – Glasstone and Hickling[37]) and of diethyl succinate (from the monoester of malonic acid – Hickling and Westwood[6]) depends on the anode material.

TABLE 1.

Anode	Smooth Pt	Platinised Pt	Au	Ni	Retort carbon	Graphite	PbO_2
Yield of ethane, %	89	3	0	0	21	4	0
Yield of diethyl succinate, %	74	0	12	0	26	35	0

TABLE 2.

Current density, A/dm²	Yield of ethane, %	Current density, A/dm²	Yield of diethyl succinate, %
0.5	52	1.0	40
2.5	71	5.0	48
5.0	77	10	68
25.0	89	20	76
50.0	89	50	74
		100	69
		200	66

2) Effect of Current Density

In the electrolysis of solutions of acetic acid and its salts, increase of current density usually favours the synthesis[44]. According to Glasstone and Hickling[45] the optimum current density for a smooth platinum anode in a solution containing equimolar quantities of acetic acid and potassium acetate is 25 A/dm². A further increase of current density does not increase the yield of ethane. A solution containing equimolar quantities of monoethyl malonate and of its potassium salt shows similar behaviour[6] (Table 2).

3) Effect of Temperature

As a rule the yield of ethane on electrolysing acetic acid – acetate solutions falls with increasing temperature[36,46,47]. Thus for a 20% solution of potassium acetate, the yield of ethane decreases from 83% at 0° to 12% at 95°;[36,46] for a 5% solution at 25 A/dm², the yield falls from 88.2% at 13° to 0.8% at 92°, and at 100° no ethane is formed[44]. In other words, the adverse effect of raising the temperature becomes more obvious the more dilute the solution.

The yield of diethyl succinate on electrolysis of aqueous potassium ethyl malonate[6] was 74% at 10° and only 22% at 90°; the current density was 50 A/dm² in both cases.

TABLE 3.

Added salt	Yield, % ethane	Yield, % diethyl succinate	Mobility of anions
Without additive	71	70	—
KF	30	47	47
$KClO_4$	20	20	64
KNO_3	19	23	62
KH_2PO_4	17	22	—
KCl	5	19	65
K_2SO_4	3	11	69
$K_3Fe(CN)_6$	0	8	97

4) Effect of Foreign Anions

Foreign anions inhibit the principal anodic reaction and their presence leads to the formation of by-products. In particular, methanol is formed instead of ethane (Hofer–Moest reaction[9,10,48]) when aqueous solutions of alkali-metal acetates are electrolysed in the presence of bicarbonates, sulphates, and perchlorates. The presence of foreign ions in the acetic acid solution may explain why some investigators did not succeed in preparing ethane by the Kolbe synthesis[49,50]. Glasstone, Hickling, and Westwood[6,37] have made a detailed study of the effect of such anions on the electrolysis of solutions of acetic acid and monoethyl malonate; the results are set out in Table 3.

The authors conclude that the inhibiting effect on the Kolbe synthesis increases with the mobility of the anion, and is considerably weaker in the electrolysis of solutions of salts of organic acids than in the electrolysis of aqueous solutions of the free acids.

5) Effect of Cations

The presence of certain metallic cations (Pb^{2+}, Mn^{2+}, Cu^{2+}, Fe^{2+}, and Co^{2+}) in relatively small amounts strongly affects the course of the Kolbe reaction in solutions of alkali-metal acetates, reducing the yield of ethane and in

** Some previously published reviews and monographs[28-34] were consulted when compiling the present survey.

several cases completely suppressing its formation[37,51]. For example, the addition of 0.001 M lead acetate to a solution containing acetic acid and potassium acetate in equimolar amounts reduces the yield of ethane from 70% to zero at current density 2.5 A/dm^2.[51] The effect of the cations follows the order $Pb'' > Mn'' > Cu'' > Co'' = Fe''$ and is especially marked at low current densities. Analogous results were obtained when the same cations were added to potassium ethyl malonate[6].

However, the Kolbe synthesis is not inhibited by the presence of many other metal cations. Glasstone and Hickling[37] obtained ethane in satisfactory yields in the electrolysis of potassium, sodium, calcium, barium, and other acetate solutions (Table 4).

TABLE 4.

Cation	Na^+	K^+	NH_4^{+*}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Mg^{2+}	Zn^{2+**}	Ni^{2+}	UO_2^{2+}
Yield of ethane, %	80	89	86	85	82	75	79	71	74	78

* Some acetamide, methylamine, and urea[154] were also found on electrolysis of ammonium acetate solution.

** In some cases, a theoretical yield of ethane was obtained on electrolysis of zinc acetate solution[53].

6) Effect of the pH of the Medium

The principal reaction product is usually formed when the pH of the electrolyte is low, its yield falling with increasing pH.[54,55]. According to Glasstone, Hickling, and Westwood[6,45], the optimum pH values lie within the limits 3–5 (Table 5); the yield of the product decreases rapidly in an alkaline electrolyte (at pH > 10).

TABLE 5.

pH	Yield of ethane, %	pH	Yield of Diethyl succinate, %
2.3	67	1.4	70
4.3	70	2.9	75
4.7	77	3.5	74
5.2	74	4.8	74
9.5	71	7.0	70
11	50	8.3	64
	—	10	59

7) Effect of Concentration

Increased concentration of carboxylic-acid anions usually leads to higher yields of the principal condensation product[44,54,55], the extent of side reactions increasing as the concentration is lowered. For example the yield of ethane decreases during the electrolysis of dilute potassium acetate solutions, more ethylene and methane being formed[56,57]. Data[6,37] illustrating the effect of concentration are set out in Table 6.

TABLE 6.

Acetate ions, M	Yield of ethane %	Ethylmalonate ions, M	Yield of diethyl succinate, %
0.2	44	0.2	30
1.0	64	0.5	68
2.0	77	1.0	70
4.0	77	2.0	74
		4.0	78

ELECTROLYTIC CONDENSATION IN NON-AQUEOUS SOLVENTS

The first experiments on the use of ethanol, propanol, and butanol as solvents in the electrolysis of acetates were carried out in 1886[58]. The electrolysis of potassium acetate in glacial acetic acid was investigated in 1904.[59,60] Further experiments were carried out on the electrolysis of acetates, propionates, and formates in anhydrous acetic, propionic, and formic acids[19]. Detailed studies proved[40,44,56,61,62] that the anode material, current density, temperature, etc., have little effect on the yield of the product in the electrolysis of solutions of carboxylic-acid salts in non-aqueous solvents. Thus, the electrolysis of a potassium acetate solution in anhydrous acetic acid gives better yields of ethane when a gold or graphite anode is used instead of a platinum anode[44]; the ratio $C_2H_6 : H_2$ equals 0.96 for a platinum anode, 0.95 for a gold anode, and 0.89 for a graphite anode; the addition of even 1% of water to the electrolyte, when a gold anode is used decreases the yield of ethane to 65%; the yield falls to 1.6% in the presence of 10% of water. Similar results were obtained in the electrolytic condensation of potassium propionate dissolved in anhydrous methanol[40].

Detailed studies of the electrolysis of potassium acetate[63] and ethyl malonate[7] in an ethylene–glycol solution have also shown that only slight variations occurred in the yield of the principal product in the presence of foreign cations and anions, and when the anodic current densities, concentration, temperature, and anode material were varied.

In large-scale electrolysis these advantages are offset by difficulties due to the low electrical conductivity of the solutions and high voltage required when working in non-aqueous solvents.

EFFECT OF THE STRUCTURE OF ACIDS ON THE COURSE OF THE KOLBE SYNTHESIS

Numerous investigations have shown that the yield of the product in the Kolbe reaction is not only affected by the conditions of electrolysis mentioned above but also to a considerable degree by the structure of the acids condensed. Thus, α-substituted carboxylic acids, cannot, in general, be subjected to the Kolbe reaction or enter into the reaction only with great difficulty. The same applies to α,β- and β,γ-unsaturated acids. Consequently, the structure of the initial acids or carboxylic-acid esters has to be considered before using them in electrolytic-condensation reactions.

The behaviour of various acids, in relation to their structure, during electrosynthesis reactions is described below. The data (unless otherwise indicated) refer to the electrolysis of aqueous solutions of sodium or potassium salts of carboxylic acids, usually in the presence of free acids.

1) Saturated Straight-Chain Acids

Fatty acids with straight C-chains of varying lengths have been subjected to the Kolbe electrolytic-condensation reaction, and normal synthesis products in satisfactory yields have been obtained in all cases, with the exception of formic acid. Many investigators have failed in attempts to produce hydrogen as well as CO_2 at the anode, according to the Kolbe reaction, on electrolysing formic acid and its salts. CO_2 or CO_2 and oxygen usually appear at the anode and the hydrogen formed is oxidised[19,64-76] to water.

Some metals of the platinum group (rhodium[77-79], palladium[80-81] and especially osmium[82]) cause formic acid to decompose as follows:

$$HCOOH \rightarrow H_2 + CO_2.$$

Although this reaction suggests that electrodes made of these metals could be used in the electrolysis of formic acid, in actual experiments hydrogen did not appear at the anodes [83].

It has been mentioned above that yields of ethane (over 90%)* are obtained on electrolysing acetic acid or its salts under similar conditions. The values of the anode potentials have been measured in numerous investigations [37,41,85,86]. Experiments have been carried out on the electrolysis of acetates with alternating current [75,76,87-91], on the electrolysis of molten acetates [88,92-95], and on the acetates of various metals [53,96-102]. The electrolytic condensation of deuterated acetates and acetic acid, in ordinary and heavy water [103-105], has also been studied.

Many investigations have been devoted to the electrolysis of the following fatty acids: propionic [10,16,19,35,40,64,73,85,87,94,95,106-109], butyric [10,11,20,26,35,64,87,95,110], valeric [1,24], caproic [24,52,87,111-114], oenanthic [14,111,112], and caprylic [112,115] **.

On electrolysis of potassium laurate in aqueous alcohol [25] *** n-docosane $C_{22}H_{46}$ was obtained in 90% yield; under analogous conditions myristic and palmitic acids [25,117] gave the corresponding n-hexacosane (up to 89% yield) and n-triacontane (up to 88% yield). Pentadecanol and pentadecane are formed as by-products in the electrolysis of palmitic acid [21,22]. Stearic acid gives a 73.6% yield of n-tetratriacontane [25]; other workers [118,119] have also investigated this reaction.

2) Half-Esters of Dibasic Acids

Earlier it was shown that alkali-metal salts of dicarboxylic-acid monoesters react, on electrolysis, similarly to monobasic fatty acids and give diesters in high yields; an exception is the monoester of oxalic acid [120] which yields hydrogen, carbon dioxide, and ethylene on electrolysis.

The method proved to be very satisfactory for the production of up to C_{34} normal dicarboxylic acids. The optimum conditions are similar to those for the synthesis of ethane: high concentration of the electrolyte solution, low temperature, high anodic current density, etc. Table 7 shows the yields obtained.

3) Branched-Chain Acids and Half-Esters

The position of the substituent in alkyl-substituted acids affects the yield of the end product of the Kolbe reaction to a considerable extent. Branching of the chains in the α-position to the carboxylic group gives rise to the formation of olefins, alcohols, and other by-products; on electrolysis such acids or half-esters give a small yield or no yield of the required product. Thus, isobutyric acid gives only small quantities of 2,3-dimethylbutane, the predominant product being propylene; isopropyl alcohol and isopropyl butyrate are formed at the same time [26,35,64].

Electrolysis of α-methyl butyric acid gives negligible quantities of 3,4-dimethylhexane and leads to formation of but-2-ene, trimethyl carbinol, and its α-methylbutyric-acid ester [25] *.

Pivalic acid, in an analogous manner, yields predominantly isobutylene and but-2-ene and only insignificant quantities of hexamethylethane [24].

Swann [152] was unable to identify the desired reaction product on electrolysing α-methylvaleric acid and α-ethylbutyric acid. Later, more accurate investigations [153] on the electrolytic condensation of the latter acid made it possible to separate tetraethylethane together with other compounds (pent-2-ene, pentan-2-ol, pentan-3-one, etc.). It has also been shown that 17,18-dibutyltetratriacontane can be prepared by the electrolysis of α-butylstearic acid [154].

Monoesters of dicarboxylic acids, containing alkyl substituents in the α-position to the carboxyl group, behave similarly. Thus, the ethyl esters of methylmalonic, ethylmalonic, dimethylmalonic [120], diethylmalonic [120,155], and dipropylmalonic [156] acids give on electrolysis small yields of the products.

It is possible to prepare the diethyl ester of $\beta,\beta,\beta'\beta'$-tetramethyl adipic acid (5–8% yield) by electrolysing the monoethyl ester of α,α-dimethyl succinic acid in methanol [157]. More satisfactory results are obtained with β-, γ-, δ-, etc. mono- and dialkyl-substituted acids. Table 8 gives data on the Kolbe reaction with acids and esters containing a branched chain in positions other than the α-position.

The optical activity of the asymmetric carbon atom in the β-position to the carboxyl group is preserved during the Kolbe reaction. It is therefore possible to use the electrochemical method to prepare stereoisomers of the dimethyl ester of β,β'-dimethylsuberic acid, with an approximate yield of 70%, from the $L(+)$- and $D(-)$-methyl esters of β-methylglutaric acid [159].

4) Unsaturated Acids

Numerous investigations have proved that neither α,β- nor β,γ-unsaturated acids undergo electrolytic condensation. The former acids give small quantities of acetylenes on electrolysis; thus acetylene is formed from acrylic acid [164], and allylene and but-2-yne respectively from crotonic [165,166] and tiglic acids [167]. Negative results were obtained on electrolysis of fumarates [120,168], maleates [120,169], citraconates [120], esters of allylmalonic [120] and muconic acids [168].

Fichter and Holbro [170] carried out experiments on the electrolytic condensation of β,γ-hexenoic acid and obtained negative results; they ascertained at the same time that γ,δ-hexenoic acid gave the normal condensation product deca-2,8-diene, in addition to by-products (penta-1,3-diene, pent-2-ene-5-ol, and its hexenoic-acid ester).

The normal condensation product was obtained (55% yield) on electrolysis of 4-ethoxycarbonyl-3-methylbut-3-enecarboxylic acid [163] in methanol:

$$2C_2H_5OOCCH{=}C(CH_3)CH_2CH_2COOH \rightarrow [C_2H_5OOCCH{=}C(CH_3)CH_2CH_2]_2 .$$

Satisfactory results were also obtained with unsaturated acids in which the double bond is further removed from the

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* In some cases [84] the electrolysis of an acetic acid solution differed from the usual course of the process.

** The yield of the principal condensation product has not been given.

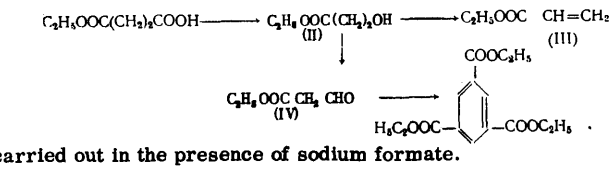
*** In one investigation methyl laurate was obtained on electrolysis of potassium laurate in boiling methanol, in the presence of potassium chloride (graphite anode, 3.5A, 90V) [116].

* The inactive 3,4-dimethylhexane formed on electrolysis of *d*- and *l*-α-methylbutyric acids [150], together with the inactive butan-2-ol and its α-methylbutyric acid ester [151].

TABLE 7. Kolbe reaction for half-esters of dicarboxylic acids with a straight $ROOC(CH_2)_nCOOH$ chain.

Initial half-ester			Solvent	Main product	By-products	Yield of main product, %	Reference
R	n						
C_2H_5	1	Ethyl malonate	H_2O	$H_5C_2OOC(CH_2)_2COOC_2H_5$	—	60	5
CH_3	2	Methyl succinate	CH_3OH	$H_3COOC(CH_2)_4COOCH_3$	ester $C_{12}H_{20}O_8$ probably $H_3COOC(CH_2)_2CH(CH_2COOCH_3)CH_2CH_2COOCH_3$	76	121
C_2H_5*	2	Ethyl succinate	H_2O	$H_5C_2OOC(CH_2)_4COO_2H_5$	—	35	5
					—	50	123
$C_6H_5CH_2$	2	Benzyl succinate	CH_3OH	$C_6H_5CH_2OOC(CH_2)_4COOCH_2C_6H_5$	—	50	124
CH_3	3	Methyl glutarate	CH_3OH	$H_3COOC(CH_2)_3COOCH_3$	—	62	125
C_2H_5	3	Ethyl glutarate	H_2O	$H_5C_2OOC(CH_2)_3COOC_2H_5$	—	28	5
$C_6H_5CH_2$	3	Benzyl glutarate	CH_3OH+ $+C_5H_5N$	$C_6H_5CH_2OOC(CH_2)_3COOCH_2C_6H_5$	—	24	126
CH_3	4	Methyl adipate	CH_3OH	$H_3COOC(CH_2)_4COOCH_3$	—	51—61	127
			CH_3OH	$H_3COOC(CH_2)_4COOCH_3$	—	74.3	129
			CH_3OH	$H_3COOC(CH_2)_4COOCH_3$		29	115**
C_2H_5	4	Ethyl adipate	H_2O	$H_5C_2OOC(CH_2)_4COO_2H_5$	$CH_2=CH(CH_2)_2COOC_2H_5$	—	129
CH_3	5	Methyl pimelate	CH_3OH	$H_3COOC(CH_2)_{10}COOCH_3$	—	47	127
							130
C_2H_5	5	Ethyl pimelate	H_2O	$H_5C_2OOC(CH_2)_{10}COOC_2H_5$	$H_5C_2OOC(CH_2)_8CH=CH_2$	—	131
						—	
CH_3	6	Methyl suberate	CH_3OH	$H_3COOC(CH_2)_{12}COOCH_3$	—	44	127
							132
C_2H_5	6	Ethyl suberate	C_2H_5OH + H_2O	$H_5C_2OOC(CH_2)_{12}COOC_2H_5$	$CH_2=CH(CH_2)_4COOC_2H_5$	— 25	5
CH_3	7	Methyl azelate	CH_3OH	$H_3COOC(CH_2)_{14}COOCH_3$		54	127
C_2H_5	7	Ethyl azelate	H_2O	$H_5C_2OOC(CH_2)_{14}COOC_2H_5$		21	133
			H_2O	$H_5C_2OOC(CH_2)_{14}COOC_2H_5$	$CH_2=CH(CH_2)_5COOC_2H_5$	—	134
C_2H_5	7	Ethyl azelate #II	H_2O	$H_5C_2OOC(CH_2)_{14}COOC_2H_5$	—	38—40	135
			CH_3OH	$H_5C_2OOC(CH_2)_{14}COOC_2H_5$	—	45	136
			C_2H_5OH+ $+H_2O$	$H_5C_2OOC(CH_2)_{14}COOC_2H_5$	$CH_2=CH(CH_2)_5COOC_2H_5$	—	132
CH_3	8	Methyl sebacate	CH_3OH	$H_3COOC(CH_2)_{16}COOCH_3$	—	42	127
			CH_3OH	$H_3COOC(CH_2)_{16}COOCH_3$	—	66	137,138
C_2H_5	8	Ethyl sebacate	H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	20	5
			H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	$CH_2=CH(CH_2)_6COOC_2H_5$	20—40	120
			H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	30—35	139
			H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	$CH_2=CH(CH_2)_6COOC_2H_5$ } $H_5C_2OOC(CH_2)_8COOC_2H_5$ }	18—25	140
			H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	—	141
			H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	44—48	142
			H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	16,5	143
			H_2O	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	—	144
			CH_3OH	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	32	145
			CH_3OH	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	—	136
			CH_3OH	$H_5C_2OOC(CH_2)_{16}COOC_2H_5$	—	65	137
C_2H_5	9	Ethyl nonane-1,9-dicarboxylate	CH_3OH	$H_5C_2OOC(CH_2)_{15}COOC_2H_5$	—	—	146
CH_3	10	Methyl decane-1,10-dicarboxylate	CH_3OH	$H_3COOC(CH_2)_{20}COOCH_3$	$CH_2=CH(CH_2)_8CCOCH_3$, probably	43	147
			CH_3OH	$H_3COOC(CH_2)_{20}COOCH_3$	$CH_3OOC(CH)_{20}COOCH_3$ —	—	146
C_2H_5	10	Methyl decane-1,10-dicarboxylate	H_2O+ $+C_2H_5OH$	$H_5C_2OOC(CH_2)_{20}COOC_2H_5$	$CH_2=CH(CH_2)_8COOC_2H_5$	41	132
CH_3	11	Methyl brassylate	CH_3OH	$H_3COOC(CH_2)_{22}COOCH_3$	$CH_2=CH(CH_2)_9COOCH_3$		148
C_2H_5	12	Ethyl dodecane-1,12-dicarboxylate	H_2O+ $+C_2H_5OH$	$H_5C_2OOC(CH_2)_{24}COOC_2H_5$	—	5.1	132
CH_3	14	Methyl tetradecane-1,14-dicarboxylate	CH_3OH	$H_3COOC(CH_2)_{28}COOCH_3$	$H_3COOC(CH_2)_{14}COOCH_3$	6	146
C_2H_5	14	Ethyl tetradecane-1,14-dicarboxylate	CH_3OH	$H_5C_2OOC(CH_2)_{28}COOC_2H_5$	—	10	146
			C_2H_5OH+ $+H_2O$	$H_5C_2OOC(CH_2)_{28}COOC_2H_5$	—	4.7	132
C_2H_5	16	Ethyl hexadecane-1,16-dicarboxylate.	C_2H_5OH+ $+H_2O$	$H_5C_2OOC(CH_2)_{32}COOC_2H_5$	—	61	149

* The cyclic ester of trimesic acid is formed in the electrolysis of monoethyl succinate[122]. The authors assume that, the ester of β-hydroxypropionic (II) and acrylic (III) acids are formed according to the Hofer-Moest reaction; (II) is oxidised at the anode to the formalacetate (IV), which is then condensed to the trimesate (V):



** The electrolysis is carried out in the presence of sodium formate.

carboxyl group, such as undec-10-enoic [112,165,171,172], petroselinic [173], oleic [166,173-175], erucic [173], and ricinoleic [175,176].

The use of the Kolbe synthesis was further extended by Bounds et al. [171], who found that the geometrical configuration at the double bonds was preserved during the electrolysis of acids of the ethylene series; thus unsaturated compounds with known geometrical configuration can be synthesised by the electrochemical method. In the electrolytic condensation of oleic and elaidic acids in absolute methanol the authors obtained the corresponding *cis*–*cis*-tetratriaconta-9,25-diene (23% yield) and *trans*–*trans*-tetratriaconta-9,25-diene (44% yield).

In the electrolytic condensation of unsaturated acids the anode generally becomes coated with a layer of insoluble polymers which are formed during the reaction and inhibit it, especially when the acids contain several double bonds [177]. A large quantity of polymeric products separates during the electrolytic condensation of the monomethyl ester of dec-5-ene-1,10-dicarboxylic acid [178]; only small yields of the normal product (eicosa-5,15-diene-1,20-dicarboxylic acid) were obtained.

5) Aliphatic Hydroxy- and Alkoxyacids

Aliphatic hydroxyacids are not very suitable for the Kolbe reaction as the hydroxyl group is readily oxidised, especially when it is adjacent to the carboxyl group. Alkoxyacids are more stable.

On electrolysis, α-hydroxy- and α-alkoxyacids (e.g. glycolic [179], methoxy- and ethoxyacetic acids [180-182], α-hydroxyoenanthic acid [182], lactic [180,183,184], α-hydroxybutyric, and α-hydroxyisobutyric acids [180]) give an aldehyde or ketone as well as an acid containing one carbon atom less than the starting material. Lactic acid has thus been converted to pyruvic acid [185].

When the monoethyl esters of ethoxymalonic and symmetrical diethoxysuccinic acid were electrolysed [182], only small quantities of the condensation product (the diethyl ester of diethoxysuccinic acid) were separated in the first case, and none at all in the second case.

Negative results were obtained on electrolysing β-hydroxyacids; electrolytic condensation of hydracrylic acid [180,186], for example, only resulted in the formation of oxidation products (formic acid, CO_2, etc.). Formic acid, crotonaldehyde, and other oxidation products are obtained from β-hydroxybutyric acid [180].

β-Alkoxyacids undergo the Kolbe reaction; the diisopentyl ether of butane-1,4-diol (50% yield) was prepared by electrolysing β-isopentyloxypropionic acid [187,188]*.

In the electrolysis of γ-pentyloxybutyric acid [190] it was found that hydrolysis replaced the Kolbe reaction, leading to the formation of pentyl alcohol and γ-hydroxybutyric acid. In the electrolysis of γ-ethoxybutyric acid [191] it was possible to separate the diethyl ether of hexanediol (20% yield). Further electrolytic condensation experiments have been carried out with 4,8-dimethyl-9-ethoxynonanoic acid in anhydrous methanol [158] and 2,6,11,15-tetramethyl-1,16-diethoxyhexadecane was formed.

Satisfactory results were obtained by electrolysis of water-alcohol and alcoholic solutions of ricinoleic [175,176] and dihydroxystearic acids [176]. The electrolysis of (±)-*threo*-9,10-dihydroxystearic and (±)-*erythro*-9,10-dihydroxy stearic acid in absolute alcohol [171] gave the corresponding diastereoisomers of the tetrol in 50% and 20% yields respectively.

Attention should also be drawn to electrolytic condensation experiments with glyceric [180], β-methylglyceric, and β-methylglycidic acids [192], as well as with the *d*-tartaric-acid monoethyl ester [193]; they all gave negative results, as only oxidation products of the initial acids were formed.

In 1908 Neuberg [194] attempted to produce polyglycols by the electrolysis of aldonic acids (*d*-gluconic, *l*-arabonic, *i*-erythronic, and *i*-glyceric acid) and glycolic acid; however, aldehydes, apparently the decomposition products of the initial acids, were separated instead of the required condensation products:

$$CH_2OH(CHOH)_xCHO \mid HCOOH \rightarrow CH_2OH(CHOH)_xCHO + HCOOH.$$

By this method glucose can be converted stepwise to formaldehyde. It can be assumed that keto-acids of the type $CH_2OH(CHOH)_xCOCOOH$ are formed as by-products.

Electrolytic decomposition has also been used in conjunction with other carboxylic-acid derivatives of sugars, e.g. melibionic acid [195].

6) Aldo-Acids

Free aldo-acids are readily oxidised in the presence of oxygen and therefore, cannot be subjected to electrolytic condensation. However, their derivatives, the acetals, are stable under electrolysis conditions.

On electrolysing an aqueous solution of the potassium salt of β,β-diethoxypropionic acid (Pt anode, Ni cathode, 3A, 8–10 V) a 60% yield of bis-diethylacetal of succinaldehyde [196]* was obtained. Analogous experiments with the potassium salt of γ,γ-diethoxybutyric acid led to the formation of the bis-diethylacetal of adipaldehyde (35% yield); acrolein acetal was also formed in this reaction.

The bis-dimethylacetal of hexadecane-1,16-dial was obtained by electrolysing 9,9-dimethoxynonanoic acid in anhydrous methanol (3–4 A, 40–50 V, 50°–55°); under similar conditions 10,10-dimethoxydecanoic acid yielded the bis-dimethylacetal of octadecane-1,18-dial [198].

It is very difficult to prepare dialdehydes by purely chemical methods.

7) Keto-Acids

In the electrolytic condensation of keto-acids, the yield of the end product depends to a considerable degree on the position of the CO group in the molecule of the initial acid, Thus pyruvic acid, the simplest keto-acid, gives only small yields of butane-2,3-dione; the principal reaction consists in the oxidation of the keto-acid to acetic acid and carbon dioxide [199]. Electrolysis of a water–alcohol solution of pyruvic acid, in an electrolyser comprising a diaphragm,

* Experiments on a similar reaction via the thermal decomposition of di (β - isopentyloxypropionyl) peroxide were carried out by Fichter and Schnider [189].

* The electrolysis of β,β-diethoxypropionic acid was described by Japanese investigators [197].

TABLE 8. Kolbe reaction for acids and half-esters with branched chains.

Initial reactant	Solvent	Main product	By-products	Yield of main product	Reference
Isovaleric acid	H_2O	$H_3C\diagdown CH-CH_2-CH_2-CH_2\diagup CH_3$ (H_3C, CH_3)	Isobutyl isovalerate, trimethylcarbinol, isobutyl alcohol, isobutyl aldehyde, 2-methylpropane, but-2-ene	—	24
Isocaproic acid	»	$H_3C\diagdown CH-(CH_2)_4-CH\diagup CH_3$ (H_3C, CH_3)	—	20	152
4,8-Dimethyl-9-ethoxynonanoic acid	CH_3OH	$[C_2H_5OCH_2CH(CH_3)(CH_2)_3CH(CH_3)CH_2CH_2]_2$	—	—	158
10-Methyloctadecanoic acid	H_2O+ +C_2H_5OH	$CH_3(CH_2)_7CH(CH_3)(CH_2)_{16}CH(CH_3)(CH_2)_7CH_3$	—	8,3	119
Ethyl β,β-dimethyl succinate *	CH_3OH	$H_5C_2OOC-C(CH_3)_2CH_2CH_2C(CH_3)_2COOC_2H_5$	Ethyl β,β-dimethylacrylate, diethyl ester of asymmetric dimethylsuccinic acid, monoethyl ester of asymmetric dimethylsuccinic acid	32—35	157
Methyl β-methylglutarate	CH_3OH+ +H_2O	$CH_3OOCCH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_2COOCH_3$	—	80	159
Ethyl β,β-dimethylglutarate	H_2O	$H_5C_2OOCCH_2C(CH_3)_2CH_2CH_2C(CH_3)_2CH_2COOC_2H_5$	—	42	160
Methyl β,β-dimethylglutarate	CH_3OH+ pet. ether	$H_3COOCCH_2C(CH_3)_2CH_2CH_2C(CH_3)_2CH_2COOCH_3$	—	75	161
Methyl methyladipate	CH_3OH	Dimethyl dimethylsebacate	—	78	162
Ethyl γ-methyladipate	CH_3OH	$H_5C_2OOCCH_2CH(CH_3)(CH_2)_4CH(CH_3)CH_2COOC_2H_5$	—	70	163
Methyl $\beta,\beta,\beta',\beta'$-tetramethylsuberate	CH_3OH+ pet. ether	$[H_3COOC\cdot CH_2\cdot C(CH_3)_2(CH_2)_2C(CH_3)_2CH_2]_2$	—	75	164
Ethyl 3,7-dimethylnonane-1,9-dicarboxylate	CH_3OH	$[H_5C_2OOCCH_2CH_2CH(CH_3)(CH_2)_3CH(CH_3)CH_2CH_2]_2$	Ethyl dimethyl-4,8-decanoate, ethyl 4,8-dimethyldec-9-enoate	48	164

* Here and subsequently the position of the substituent is given in relation to the free carboxyl group.

and graphite, platinum, or lead anodes, gave in all cases lactic[200] as well as acetic acid.

The monoethyl ester of acetone dicarboxylic acid[201] has been electrolysed yielding the diester of hexane-2,5-dione-1,6-dicarboxylic acid (12% yield).

Considerably better results were obtained in the electrolysis of aqueous solutions of levulinic acid[199] in which the normal product, octane-2,7-dione, was obtained in 50% yield. When this process is carried out in a 25% sulphuric-acid solution or in methanol, the yield increases to 66% and 70% respectively[202].

The electrosynthesis process is also favoured by increasing the distance between the keto- and the carboxyl group in the keto-acid molecule. Thus tetradecane-3,12-dione, the normal product, was obtained in 74.8% yield on electrolysis of δ-propionylvaleric acid[203].

8) Halogeno-Substituted Acids

Up to 1956 very little was published on the possibility of using the Kolbe reaction for the synthesis of halogeno-substituted compounds. Kaufler and Herzog[204] discovered in 1909 that electrolysis of chloro*-, bromo- and iodoacetic acids did not give products of the Kolbe reaction. Negative results were also obtained in the electrolysis of dichloro-[204,205], difluorochloro-[207], and trichloroacetic[208-211] acids. Only the electrolysis of trifluoroacetic acid gave traces of hexafluoroethane[207,212]. Unsatisfactory results were also obtained in attempts at synthesis from α,α-dichloropropionic[205], β-iodopropionic[205], 2,2,3-trichlorobutyric[213], and *d,l*-α-bromopropionic acids[214]. Japanese investigators[177] were also unsuccessful when they electrolysed tetrabromostearic acid in ethanol.

In 1953 Korsching[215] succeeded in isolating the normal product (1,20-dibromoeicosane, 20% yield) in the electrolysis of 11-bromoundecanoic acid; later[216] he succeeded in preparing 1,10-dibromodecane from ω-bromocaproic acid in a water-alcohol solution.

Detailed investigations on the electrolytic condensation of ω-halogenocarboxylic acids, carried out in 1956,[137] showed that normal products are obtained when β-chloropropionic, δ-chlorovaleric, 6-chlorohexanoic and 10-chlorodecanoic are electrolysed in absolute methanol (11–16 A/dm², 2 A, 110 V, 50°), in contrast to the reaction for chloroacetic and γ-chlorobutyric acid.

Halogen is split off during the electrolysis of lower ω-bromocarboxylic acids. Normal condensation reactions could only be observed with acids containing 11 or more carbon atoms in the chain. All ω-iodocarboxylic acids (containing 2–11 carbon atoms in the molecule) decompose on electrolysis. ω-Fluorocarboxylic acids give considerably better results. The lower members of this series (fluoroacetic, β-fluoropropionic, and γ-fluorobutyric acid) do not undergo the Kolbe reaction; the glass electrolyser is attacked – an indication that hydrogen fluoride is evolved in the process. However, δ-fluorovaleric, 6-fluorohexanoic, 7-fluoroheptanoic, 8-fluorooctanoic, 9-fluorononanoic 10-fluorodecanoic, and 11-fluoroundecanoic acids give satisfactory yields of ω,ω'-difluoroalkanes.

* See also refs. 92, 205, and 206 on the electrolysis of chloro-acetic acid.

Thus electrolytic condensation proves to be a convenient method for synthesising C_8 and higher dilfuorides and dichlorides as well as C_{20} and higher dibromides.

The yields of the products of electrolysis of ω-halogenocarboxylic acids are given in Table 9.

TABLE 9. Electrolysis of ω-halogencarboxylic acids $[X(CH_2)_nCOOH]$.

n	Yield, %			
	F	Cl	Br	I
1	0	0	0	0
2	0	39	0	0
3	0	0	0	0
4	45	51.5	0	0
5	45	55	0	0
6	57.5	—	—	—
7	64	—	0	—
8	65	—	—	—
9	69	82	0	0
10	61	—	54	0
15	—	—	31	—

9) Amino-Acids

Lilienfeld[217] found in 1902 that ethylene diamine is formed on electrolysis of the copper salt of glycine, but later investigators[218-220] failed to confirm this.

The Kolbe reaction did not occur and complete destruction of the original molecule was observed in the electrolysis of other α- or β-amino-acids (α-alanine and leucine[220], aceturic acid, β-alanine, iminodiacetic acid, methylaminodiacetic acid, and α-aminoisobutyric acid[219]. Later it was proved[221] that the corresponding alkoxyalkylamides are formed when α-amino-acids are electrolysed in anhydrous alcohol in the presence of an alcoholate:

$$R_1CONH\cdot\underset{\displaystyle X}{\underset{|}{CH}}\cdot COOH + R_2OH \rightarrow R_1CO\cdot NH\cdot\underset{\displaystyle X}{\underset{|}{CHOR_2}} + CO_2,$$

where X = H or CH_3.

In 1947 Offe[222] established that aliphatic diamines or their derivatives can be synthesised by the Kolbe reaction under the following conditions: (1) the basic properties of the amino-group have to be weakened; (2) electrolysis of the amino-acid acid salt has to be carried out in a non-aqueous solvent; (3) the amino-group must not be in the α-position to the carboxyl group. He prepared *N*,*N*'-diacetyl decamethylene diamine* by electrolysing ε-acetylaminocaproic acid in methanol at a current density of 5–7 A/dm² at a platinum anode. Normal products were also obtained, under analogous conditions, from ε-benzoylaminocaproic, γ-phthalimidobutyric, ε-ethanesulphonylaminocaproic, ε-propanesulphonylaminocaproic acid and *N*-(5-methoxycarbonylpentanoyl)-ε-aminocaproic acid.

Unsatisfactory results were obtained with *N*-substituted benzenesulphonylamino-acids; e.g. during the electrolysis of *N*-(benzenesulphonyl)-ε-aminocaproic acid only benzene sulphonamide was separated. This confirmed the earlier observations that *N*-(*p*-toluenesulphonyl)-α-aminoisobutyric acid and *N*-(benzenesulphonyl)-*N*-methyl-α-aminoisobutyric acid do not give a Kolbe reaction[219].

Later the Kolbe synthesis was successfully carried out in methanol with many *N*-acyl-derivatives of amino-acids in which the amino-group was at a considerable distance from the carboxyl group[221]. The corresponding derivatives of polymethylene diamines were obtained in good yields (Table 10).

Satisfactory results were also obtained in the electrolysis of the half-amide of adipic acid in methanol, at a current density of 5–7 A/dm² at the anode[223,224].

Experiments were also carried out on the electrolytic condensation of cyanoacetic acid[225-226]. Only minute quantities of the normal reaction product (ethylene dicyanide) were isolated, most of the products resulting from decomposition: hydrocyanic acid, formaldehyde, carbon dioxide, etc.

10) Sulpho-Acids

The electrolysis of sulphoacetic acid should proceed according to the equation

$$2HO_3SCH_2COO^- \xrightarrow{-2e} \underset{\displaystyle HO_3SCH_2}{\overset{\displaystyle HO_3SCH_2}{|}} + 2CO_2,$$

in a manner analogous to the synthesis of ethane from acetic acid.

However, instead of ethane disulphonic acid the oxidation products of the initial compound were obtained (sulphuric acid, carbon dioxide, carbon monoxide, ethylene, formaldehyde, sulphur dioxide, and small quantities of methionic acid)[227,228].

On electrolysing β-sulphopropionic acid[228] only ethylene, sulphur dioxide, carbon dioxide, sulphuric, formic, and acetic acids were isolated*.

11) Alicyclic Acids

In their behaviour in the electrolytic condensation, cycloalkane acids resemble alkyl-substituted acids. Thus, cycloalkyl substituents in the α-position to the carboxyl group, inhibit the principal anodic reaction. An interesting example is the electrolysis of cyclopropanecarboxylic acid: the allyl ester of the initial acid is formed instead of the required bicyclopropyl[230,231].

TABLE 10.

Initial reactant	Solvent	Product	Yield, %
$CH_3CONH(CH_2)_5COOH$	CH_3OH	$CH_3CONH(CH_2)_{10}NHCOCH_3$	31
$C_6H_5CONH(CH_2)_5COOH$	CH_3OH	$C_6H_5CONH(CH_2)_{10}NHCOC_6H_5$	23
$C_6H_5CH_2OCONH(CH_2)_5COOH$	CH_3OH	$C_6H_5CH_2OCONH(CH_2)_{10}NHOCOCH_2C_6H_5$	38
$C_6H_5CH_2OCONH(CH_2)_5COOH$	CH_3OH	$C_6H_5CH_2OCONH(CH_2)_4NHOCOCH_2C_6H_5$	35
$C_6H_5CONHCH_2CH_2COOH$	CH_3OH	$C_6H_5CONH(CH_2)_4NHCOC_6H_5$	20
$C_6H_5CH_2OCONHCH_2CH_2COOH$	CH_3OH	$C_6H_5CH_2OCONH(CH_2)_4NHOCOCH\ C_6H_5$	33

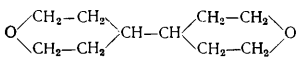
* The same compound was also obtained on electrolysis of a mixture of ε-acetylaminocaproic and formic acids in methanol[115]

* Attempts[229] at the electrolytic condensation of a number of aromatic sulphonic acids (benzene-*p*-disulphonic acid, benzene-*m*-disulphonic acid, phenyl disulphide-4,4-disulphonic acid and phenol-2,5-disulphonic acid) were also unsuccessful.

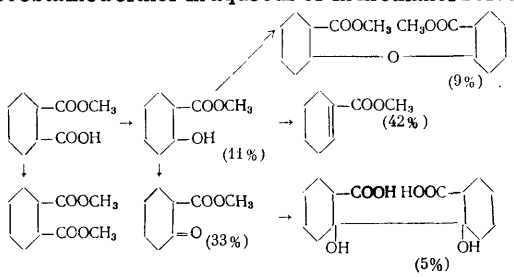
On electrolysis of the monomethyl ester of *cis*-cyclopropane-1,2-dicarboxylic-acid[232] ring cleavage occurs and the ester of hexa-2,4-diene-1,6-dicarboxylic acid* is formed. Negative results were obtained on electrolysis of cyclobutanecarboxylic acid[231,234], cyclohexanecarboxylic acid[231,235], and *p*-methylcyclohexanecarboxylic acid[236].

Later investigations of the electrolysis of cyclohexanecarboxylic acid showed that negligible quantities of the anodic-synthesis product, bi(cyclohexyl), are formed when the process is carried out in an acidic solution[237]; when a methanol-pyridine mixture is used as solvent, the yield of bi(cyclohexyl) is 14%.[238]

Satisfactory yields (20%) of 4,4-bis-tetrahydropyranyl were obtained by electrolysing an aqueous solution of the potassium salt of tetrahydropyran-4-carboxylic acid[239]; at the same time equal quantities of 4-hydroxytetrahydropyran, and its tetrahydropyran-4-carboxylic-acid ester were isolated.

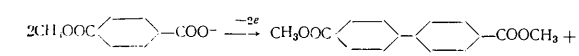


An aqueous solution of the monoethyl ester of cyclohexylmalonic acid gave, on electrolysis, α,α'-dicyclohexylsuccinic acid (a mixture of the two stereoisomers); the yield was 17%.[123] Detailed studies of the electrolysis of hexahydrophthalate showed that a number of by-products were formed (see below); the expected anodic-synthesis product was not obtained either in aqueous or in methanol solutions[240]



Later[241] it was proved that under the given conditions of electrolysis of monomethyl esters of *cis*- and *trans*-hexahydrophthalic acid in anhydrous methanol, normal condensation products, i.e. dimethyl *trans-anti-trans*- and *trans-syn-trans*-bi(cyclohexyl)-2,2'-dicarboxylate are formed, but only in small quantities; the principal reaction products are monomeric compounds – the methyl esters of cyclohex-1-ene-1-carboxylic, cyclohex-2-ene-1-carboxylic acid, and cyclohexanecarboxylic acids.

It should be pointed out that the isomeric methyl ester of *trans*-1,4-cyclohexanedicarboxylic acid gave appreciable quantities (32%) of the Kolbe-synthesis product[242]



Ester groups in the *p*-position obviously aid the electrolytic condensation.

Electrolytic condensation of several alicyclic dicarboxylic-acid esters was successfully carried out in a mixture of methanol and petroleum ether (Pt anode, 4–6 A/dm²). Thus, electrolysis of the monomethyl esters of cyclopentane-1,1-diacetic acid, 2,2,5,5-di(tetramethylene)hexane-1,6-dicarboxylic acid, cyclohexane-1,1-diacetic acid, and 2,2,5,5-di(pentamethylene)hexane-1,6-dicarboxylic acid[161] gave the dimethyl esters of the corresponding 2,2,5,5-di(tetramethylene)hexane-1,6-dicarboxylic acid, 2,2,5,5,8,8,11,11-tetra(tetramethylene)-dodecane-1,12-dicarboxylic acid, 2,2,5,5-di(pentamethylene)hexane-1,6-dicarboxylic acid (38% yield), and 2,2,5,5,8,8,11,11-tetra(pentamethylene)dodecane-1,12-dicarboxylic acid (14.5% yield).

Other investigations dealt with the electrolytic condensation of half-esters of camphoric acid[243-249].

12) Aromatic and Aliphatic-Aromatic Acids

For a long time it was assumed that salts of aromatic acids, unlike those of aliphatic acids, did not enter into the Kolbe reaction.

Experiments on the electrolytic condensation of solutions of salts of benzoic acid in water[92,250,251], sulphuric acid[252], and absolute methanol[253], and the electrolysis of fused benzoic acid[93,99] were indeed unsuccessful. The reaction products were, in general, benzene, free benzoic acid, oxygen, etc. The same was true of the electrolytic condensation of substituted benzoic acids such as *o*-nitrobenzoic[254], *p*-nitrobenzoic[217-255], *p*-toluic[236,256,257], opianic[258], salicylic, *m*-hydroxybenzoic, and *p*-hydroxybenzoic acids[92], 3,5-dimethyl- and 2,4-dimethylbenzoic acids[259], and ethyl phthalate[120].

On electrolysing 2,5-dimethyl-4-t-butylbenzoic acid in methanol[253] one of the methyl substituents in the aromatic nucleus was oxidised and, on subsequent esterification, the methyl ester of 6-methyl-4-t-butyl-1,2-phthalic acid was formed together with 1,3-dimethyl-5-t-butylbenzene.

Negative results were obtained on electrolysing some aromatic acids which contained the carboxyl group in the side chain, e.g. aqueous solutions of potassium salts of phenylacetic acid[260], diphenylacetic acid[261], and also of the ethyl ester of benzylmalonic acid[120]*.

In the 1930's Fichter et al. refuted the conclusion that aromatic acids do not undergo the Kolbe reaction. They proved that the characteristic electrosynthesis product (2,2'-diindanyl) is formed in the electrolysis of indane-2-carboxylic acid in methanol[263,264], although only in small quantities. Other aromatic acids can be electrolysed successfully by using a methanol-pyridine mixture as solvent. Thus, benzoic, phenylacetic, β-phenylpropionic, and phenoxyacetic acids[265] yielded the corresponding diphenyl, dibenzyl (50% yield), 1,4-diphenylbutane (37% yield), and the diphenyl ester of ethylene glycol (45% yield). Normal products (the respective yields being 27, 24, and 8%) were obtained on electrolysing *o*-, *m*-, and *p*-cresoxyacetic acids[267] under analogous conditions.

Under these conditions it was possible to prepare tetraphenylethane by electrolysing diphenylacetic acid[268,269], and also 1,4-diphenylbutane (34% yield), 1,6-diphenylhexane (37% yield), and 1,8-diphenyloctane (47% yield) from the corresponding β-phenylpropionic, γ-phenylbutyric, and δ-phenylvaleric acids[270].

Dibenzyl was produced in 1952 by electrolysing phenylacetic acid in anhydrous methanol and also by electrolysis of fused phenylacetic acid[266]. At the same time it was found that electrolysis of phenylacetic acid in acetic acid

* In the electrolysis of the monomethyl ester of cyclopropane-dicarboxylic acid in methanol the ester of the unsaturated dibasic acid, probably α,α'-dimethyleneadipic acid, was formed instead of the expected diester of dicyclopropanedicarboxylic acid[233].

* The diethyl ester of dibenzylsuccinic acid[262] is formed when the monoethyl ester of benzylmalonic acid is electrolysed in the presence of acetic acid.

and also of diphenyl- and triphenylacetic acids in acetic acid or anhydrous methanol caused the acetoxylation or methoxylation of the benzene nuclei respectively.

Results on the electrolysis of γ-phenylisovaleric, 3,3,3-triphenylpropionic, and 3,3,3-tri-*p*-t-butylphenylpropionic acid in methanol, using a platinum anode, were published recently[271]. Electrolysis of the first acid, in the presence of an excess of sodium acetate (15 A/dm^2, 60°) gave t-pentylbenzene (32%); 2,5-diphenyl-2,5-dimethylhexane and homologues of α-methylstyrene were separated as by-products. Electrolysis of the second acid led to the formation of the phenyl ester of 3,3-diphenyl-3-methoxypropionic acid, and the third acid gave the *p*-t-butylphenyl ester of 3,3-di-*p*-t-butylphenyl-3-methoxypropionic acid.

13) Dicarboxylic Acids

Alkali-metal salts of dicarboxylic acids do not undergo the Kolbe reaction at the anode.

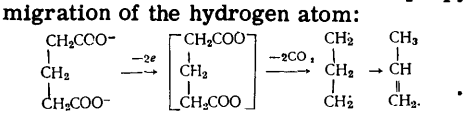
Only hydrogen, oxygen, carbon dioxide[70,73-76,272-276], and in some instances glycolic acid[277] could be detected in the electrolysis products of oxalic acid.

The higher dibasic acids (malonic to sebacic) form olefins and alcohols which contain two carbon atoms less than the original acid, and also saturated and unsaturated acids with one carbon atom less. Attempts to isolate cycloalkanes, the formation of which might be expected as 2 molecules of carbon dioxide are split off simultaneously from the dibasic-acid anion, were unsuccessful.

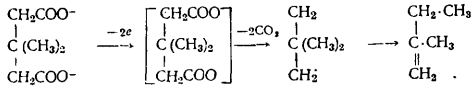
Ethylene, hydrogen, oxygen, carbon monoxide, and carbon dioxide are formed in the electrolysis of malonic acid[272,278]. Schall[279] found that in the electrolysis of the alkali-metal salts of malonic acid, hydrogen peroxide is formed on cooling, probably through the hydrolysis of the intermediate malonic-acid peroxide.

Electrolysis of succinic acid[272,280] leads to the formation of ethylene, oxygen, hydrogen, and carbon dioxide*; tartaric and oxalic acid were also isolated as oxidation products[282]. By electrolysing succinic acid in an alkaline solution in the presence of sodium perchlorate, Hofer and Moest[10] also prepared β-hydroxypropionic acid** together with acrylic acid, carbon monoxide, carbon dioxide, acetylene, acetaldehyde, methanol, and acetic and formic acids.

When an aqueous solution of the potassium salt of glutaric acid was electrolysed with the object of obtaining cyclopropane[284], the products were found instead to be propylene, carbon dioxide and oxygen. The formation of propylene is due to the migration of the hydrogen atom:



In the electrolysis of the salt of β,β-dimethylglutaric acid, where no hydrogen transfer can take place, the whole hydrocarbon group is shifted and the unsymmetrical methylethylethylene is formed[160]



The cyclic product – dimethylcyclopropane – was not formed.

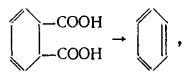
A number of higher dicarboxylic acids, such as adipic[285], pimelic[286-289], suberic[289-290], and sebacic[272] acids, have been electrolysed but in no case could the formation of cycloalkanes be detected.

14) Substituted Dibasic Acids

On electrolysis, methylmalonic acid yields ethylene, hydrogen, oxygen, and carbon monoxide and dioxide[92,272]; propylene, propanol, isopropyl alcohol, and other oxidation products[272] are formed from ethylmalonic acid and pyrotartaric acid.

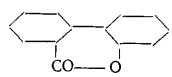
Salts of malic, tartaric, and pyrotartaric acids[291] have also been electrolysed; malic acid gave malonic acid, which was then readily oxidised to oxalic and formic acids and carbon dioxide. Formic acid was formed from the other two acids. Oxalic acid and carbon dioxide were obtained in the electrolysis of mesoxalic acid.

The preparation of benzene (70% yield) from *trans*-1,2-dihydrophthalic acid[292],



and propadiene[233] by opening the ring of 1,2-cyclopropanedicarboxylic acid on electrolysis of its salts, are isolated instances of the formation of unsaturated hydrocarbons in the electrolysis of substituted dibasic acids.

In 1957[293] *cis-syn-cis*-, *trans-anti-trans*-, and *trans-syn-trans*-perhydrodiphenic acids were electrolysed in anhydrous methanol. The principal reaction product (approx. 45%) was in all cases the corresponding isomeric γ-lactone; its structure was determined by synthesis:



15) Unsaturated Dibasic Acids

In the electrolysis of salts of fumaric[280] and maleic[169,280]* acids carbon dioxide and acetylene are formed at the anode, the maleic acid being partly converted to fumaric acid.

Acetylene, acrolein, carbon monoxide, and carbon dioxide are obtained when glutaconic acid is electrolysed[295].

Mesaconic acid[296] forms propyne, and acrylic and itaconic acids, whilst its isomers, itaconic[297-299] and citraconic[296] acids, yield propyne, and acrylic and mesaconic acids. The type of salt of the citraconic acid used in the electrolytic condensation determines the yield of propyne; thus the highest yield (52%) of propyne was obtained by electrolysing the rubidium salt of citraconic acid and the lowest yield (16%) when the lithium salt was used[300].

Fumaric acid and acetylene[301,302] have been prepared from acetylenedicarboxylic acid.

* See Fichter and Fritsch's publications[281] on the decomposition of succinic-acid peroxide to carbon dioxide and ethylene.

** β-hydroxypropionic acid and the acrylic acid formed from it were also obtained by the thermal decomposition of monopersuccinic acid[283].

* Malic acid is formed in the electrolysis of hydroxymaleic acid[294].

"CROSSED" ELECTROLYTIC CONDENSATION

In this reaction acids or half-esters of dicarboxylic acids with different radicals are caused to react. Such reactions do not take place very readily and are seldom carried out. The main difficulty lies in the fact that the condensation process can proceed equally readily in three principal ways:

$$\left.\begin{matrix}RCOO^- \\ R_1COO^-\end{matrix}\right\} \xrightarrow{-2e} R{-}R_1 + 2CO_2 ,$$

$$2RCOO^- \xrightarrow{-2e} R{-}R + 2CO_2 ,$$

$$2R_1COO^- \xrightarrow{-2e} R_1{-}R_1 + 2CO_2 .$$

As in the simple Kolbe synthesis a series of side reactions accompany the electrolysis; this explains the comparatively small yield of the main reaction product ($R-R_1$).

The reaction was first carried out by Würtz in 1855 [3,4], who succeeded in preparing a small quantity of heptane and decane by electrolysing a mixture of oenanthic and acetic acids and a mixture of oenanthic and valeric acids respectively* . It was later used by other investigators for synthesising a number of compounds. Mixtures of acids and half-esters of dicarboxylic acids with straight and branched chains were used and also carboxylic acids containing various substituents (keto- and amino-groups, halogens, etc.) and double and triple bonds in the chain.

Most publications on the "crossed" electrolytic condensation recommend that methanol solutions of potassium or sodium salts of the acids be used as electrolytes**. Electrolysis of a mixture of the methyl ester of adipic acid with acetic acid or hexanoic acid in anhydrous methanol (11–16 A/dm², 1–2 A, 110 V, 50°) yielded the corresponding methyl esters of hexanoic acid (42% yield)*** and decanoic acid (61% yield) [137].

The methyl ester of arachidic acid (41.5% yield) was obtained from the monomethyl ester of adipic and palmitic acids in boiling methanol (7 A/dm², 5.6 A, 12–38 V) [127,306] Under analogous conditions the methyl ester of adipic and stearic acids yielded the methyl ester of behenic acid (38% yield); electrolysis in methanol (4–12 A/dm², 40°–60°) of the methyl ester of adipic acid with butyric, capric, or lauric acids yielded the corresponding caprylic (30.6% yield), myristic (7% yield), and palmitic acids (23.4% yield) [304]****.

The use of benzyl esters as starting materials in place of the ethyl and methyl esters in syntheses of this kind makes it possible to avoid esterification with the methanol used as solvent, which very often accompanies "crossed" syntheses. Thus, palmitic (30% yield) and arachidic (25% yield) acids respectively [124] can be produced by condensing the benzyl ester of succinic and myristic or stearic acids in methanol (6–7 A/dm², 1–1.3 A, $t < 50°$) and hydrolysing the products.

According to other data [126] the use of monobenzyl esters as one component during the "crossed" electrolytic condensation of a mixture of half-esters of dicarboxylic acids, facilitates the isolation of the product. Thus the methyl ester of pimelic acid (24% yield) was obtained by electrolysing the benzyl ester of glutaric acid and the methyl ester of succinic acid in a methanol-pyridine mixture (Pt electrode, 0.2 A, 34 V, 35°) and subsequent hydrogenolysis of the reaction products. It has been shown [304] that addition of tetrahydrofuran is advisable in this synthesis. Electrolysis of the ethyl ester of adipic acid with myristic, pentadecanoic, and stearic acids in methanol in the presence of tetrahydrofuran (2.5–12.5 A/dm², 0.2–1 A, 40°–60°) gave the corresponding stearic (12.7% yield), nonadecanoic (6.7% yield), and behenic acids (4.7% yield).

The same rule as in simple Kolbe reactions applies here for substituted and unsaturated acids: the starting compound must not contain a branched chain, a functional group, or an unsaturated bond in the α-position to the carboxyl group. It should be pointed out, however, that Japanese chemists [307] succeeded in preparing 10-methyloctadecanoic acid by electrolysing a mixture of the ethyl ester of sebacic and methyloctalacetic acids (reaction conditions and yields are not given).

3-methylundecanoic acid (46% yield) was obtained in the electrolysis of monomethyl β-methylglutarate and octanoic acid in anhydrous methanol (10 A/dm², 2 A) [308]. The same authors synthesised the methyl ester of 10-methyloctadecanoic acid (38% yield) from the monomethyl ester of azelaic acid and 3-methylundecanoic acid (6.4–8.8 A/dm², 1.1–0.8 A); similarly, electrolysis of the monomethyl ester of γ-methyladipic acid with caproic acid gave 3-methyldecanoic acid (65% yield) [163]; electrolytic condensation of a mixture of ethyl β,β-methylethylglutarate and capric or lauric acids [309] yielded the corresponding β,β-methylethyltridecanoic and β,β-methylethylpentadecanoic acids.

Electrolysis in methanol at 10–20 A/dm² of monomethyl glutarate and 3-methylheptanoic acid, monomethyl succinate and 4-methyloctanoic acid, and the monomethyl ester of azelaic acid and 3,9-dimethyltridecanoic acid [310] yielded in the first two instances 6-methyldecanoic acid (35 and 32% yields), and in the last, 10,16-dimethyleicosanoic acid (54% yield). The same paper gives results on the "crossed" condensation when both initial acids contain branched carbon chains. Thus, 3,9-dimethyltridecanoic acid (51% yield) is formed in the electrolysis of monomethyl β-methylglutarate and 6-methyldecanoic acid. In an analogous manner 3,13,19-trimethyltrieicosanoic acid (18.5% yield) was prepared from monomethyl β-methylglutarate and 10,16-dimethyleicosanoic acid.

The electrolytic condensation of optically active substances has been very thoroughly investigated to find satisfactory methods for the synthesis of stereoisomers of compounds with branched chains of known structure. In this way it was possible to prepare D(+)-3-methylundecanoic acid (yield 35%) [311–313] by electrolysing an equimolar mixture of monomethyl L(+)-β-methylglutarate and caprylic acid in boiling methanol (Pt electrodes, 5 A, pH < 8) [311, 313].

By an analogous method L(-)-3-methylundecanoic acid (35.5% yield) was synthesised from monomethyl D(-)-β-methylglutarate and caprylic acid. Electrolysis of a mixture of the monomethyl ester of sebacic acid and D(+)-3-methylundecanoic or L(-)-3-methylundecanoic acid led to the formation of the corresponding D(+)-11-methylnonadecanoic acid (24% yield) and L(-)-11-methylnonadecanoic acid (22.5% yield). Condensation of palmitic acid with the monomethyl esters of D(+)- and L(-)-β-methylsuccinic acid gave the corresponding D(-)- and L(+)-2-methyloctadecanoic acids [314].

* Schorlemmer [303] repeated Wurtz' experiment in 1865 and obtained similar results.

** Unless otherwise stated "crossed syntheses" discussed below refer to the electrolysis of sodium and potassium salts of carboxylic acids, carried out in the presence of free acids.

*** Hexanoic acid (40.8% yield) was also obtained in the electrolysis of the monoethyl ester of adipic acid and acetic acid [304] in ethanol (10 A/dm², 0.8 A, 40°–60°).

**** See also publications by Japanese authors [306] on the electrolysis of dibasic-acid esters with fatty acids.

Higher yields can be obtained by using, in similar syntheses, an excess of the optically inactive component. In the electrolysis of caprylic acid with the monomethyl esters of L(+)- and D(-)-β-methylglutaric acid, in anhydrous methanol (molar ratio of the optically inactive to the active component 2 : 1, 2 A, 10 A/dm^2), the corresponding D(+)- and L(-)-3-methylundecanoic acids (48% yield) were obtained. Under similar conditions, the monomethyl ester of azelaic acid and D(+)- and L(-)-3-methylundecanoic acid yielded the D(-)-10-methyloctadecanoic and L(+)-10-methyloctadecanoic acids (30–31% yield)[315].

Unsaturated acids, mixed with dicarboxylic-acid esters, also undergo "crossed" electrolytic condensation. Thus pentadecenoic acid was obtained by the electrolysis of a mixture of undecenoic acid and monomethyl adipate in anhydrous methanol (0.83 A/dm^2, 80–100 V); after purification (via the methyl ester) the yield was approximately 15%.[316] In later investigations it was possible to increase the yield to 30%.[171] A number of other unsaturated acids have also been synthesised by this reaction: 3,3-dimethyltetradec-13-enoic acid[317] by the electrolysis, in ethanol, of undecenoic acid and the ethyl ester of β,β-dimethylglutaric acid (10 A/dm^2, 100 V); docos-21-enoic acid from the ethyl ester of tetradecane-1,14-dicarboxylic acid and oct-1-enoic acid[318].

When double bonds are present in the α-position to the carboxyl group unsatisfactory results are obtained; electrolysis of a mixture of acetic acid and monoethyl fumarate or monomethyl muconate in absolute methanol did not lead to the formation of the expected unsymmetrical products:

$$CH_3CH{=}CHCOOC_2H_5 \text{ and } CH_3CH{=}CH{-}CH{=}CHCOOCH_3$$[168].

Bounds et al. showed that the geometrical configuration at the double bonds was maintained in the simple Kolbe reaction. They[125,171,319] proved that the configuration at the double bonds was also preserved during the "crossed" condensation.

In the electrolysis of oleic and elaidic acids with an excess of adipic acid monomethyl ester, in anhydrous methanol (Pt electrodes, 10 A/dm^2, 1.7 A, 50°) the "crossed" products were obtained in both cases; their hydrolysis gave the corresponding erucic and brassidic acids (approximate yield 30%)[171]. Similarly, electrolysis of the monomethyl ester of suberic acid with oleic or elaidic acids[125] gave, after hydrolysis, *cis*- and *trans*-tetracos-15-enoic acids respectively (respective yields 37% and 32%). The unsymmetric product *cis*-octadec-11-enoic acid (12% yield), was obtained in the electrolysis of a mixture of *cis*-hexadec-9-enoic and monomethyl succinate[319].

Studies by American chemists[320] on the preparation of esters of unsaturated α,ω-dicarboxylic acids by electrolysing a mixture of dicarboxylic-acid esters and conjugated dienes, are of great interest. They prepared the diethyl ester of deca-3,7-diene-1,10-dicarboxylic acid by the electrolysis, in methanol, of monoethyl malonate and butadiene (Pt electrodes, 1.1 A, -5°). The diethyl ester of dodeca-4,8-diene-1,12-dicarboxylic acid, the diethyl ester of hexadeca-6,10-diene-1,16-dicarboxylic acid, and other compounds were prepared by similar methods.

Satisfactory results have been obtained in the electrolytic condensation (in methanol) of acids of the acetylenic series[321]. Stearolic acid (octadec-9-ynoic acid) (6% yield) was obtained from pentadec-6-ynoic acid and monomethyl glutarate (6–7),A/dm^2). The same acid was obtained in the electrolytic condensation of tetradec-5-ynoic acid and monomethyl adipate at 15–16 A/dm^2 (24% yield). Electrolysis of a mixture of monomethyl adipate and stearolic acid (8–10 A/dm^2), pentanoic acid and the methyl ester of dodec-6-ynoic acid (6.8–8 A/dm^2), and hexanoic acid and the methyl ester of dec-5-ynoic acid led to the formation of the corresponding docos-13-ynoic (behenolic) acid (26% yield), pentadec-6-ynoic acid (25% yield), and tetradec-5-ynoic acid (27% yield). Octadec-6-ynoic acid (23% yield) was prepared from the monomethyl ester of dec-5-yne-1,10-dicarboxylic acid and caprylic acid[178].

TABLE 11.

Initial reactants		Molar ratio I:II	"Crossed" product	Yield, % (with respect to I)
I	II			
Levulinic acid	$CH_3(CH_2)_3COOH$	1 : 1	methyl hexyl ketone	35
ditto	CH_3COOH	1 : 3	methyl propyl ketone	20
»	$CH_3(CH_2)_2COOH$	1 : 6	methyl pentyl ketone	62
»	CH_3CH_2COOH	1 : 1	methyl n-butyl ketone	20
»	$(CH_3)_2CHCH_2COOH$	1 : 1	$CH_3CO(CH_2)_2CH(CH_3)_2$	—
»	$CH_3(CH_2)_4COOH$	1 : 2	methyl n-heptyl ketone	42
»	$CH_3(CH_2)_6COOH$	1 : 1	methyl n-nonyl ketone	31
»	$CH_3(CH_2)_6COOH$	2 : 1	methyl n-undecyl ketone	24
»	$CH_3(CH_2)_{10}COOH$	2 : 1	$CH_3CO(CH_2)_{12}CH_3$	20
»	$CH_3OOC(CH_2)_2COOH$	2 : 1	$CH_3CO(CH_2)_4COOCH_3$	25–30
»	$CH_3OOC(CH_2)_4COOH$	2 : 1	$CH_3CO(CH_2)_6COOCH_3$	20
»	$CH_3OOC(CH_2)_4COOH$	4 : 1	$CH_3CO(CH_2)_6COOCH_3$	38
»	$CH_3OOC(CH_2)_8COOH$	2 : 1	$CH_3CO(CH_2)_{10}COOCH_3$	12

Halogeno-substituted acids were also subjected to this type of electrolytic condensation. Electrolysis of 10-fluorodecanoic and 5-chloropentanoic acid (Pt anode, 16 A/dm^2, 50°) in methanol gave 13-fluorotridecyl chloride (24.4% yield)[137]. Under the same conditions 10-fluorodecanoic acid and the monomethyl ester of sebacic acid gave the methyl ester of 18-fluorostearic acid (4.8% yield).

The reactions of chloroacetic acid are of great interest; in the simple Kolbe reaction only oxidation products are obtained[204–206], but on electrolysis in a mixture with other acids its behaviour is similar to that of unsubstituted acetic acid. Cetyl chloride was obtained when chloroacetic and palmitic acids were electrolysed in a water-alcohol medium at 70°–75°.[322] Unsatisfactory results were obtained when trichloroacetic acid was used instead of chloroacetic acid.

Hunsdiecker[323] did much work on the electrolytic condensation of keto-acids with fatty acids. He prepared dodeca-2,5-dione (30–45% yield) by the electrolysis of a mixture of 4,7-diketooctanoic and caproic acids in anhydrous methanol (3–5 A, 50–90 V). 4,7-Diketooctanoic acid was also reacted, under analogous conditions, with propionic, butyric, valeric, isovaleric, caprylic, and lauric acids, and also with monomethyl succinate and adipate. Unsymmetrical products were obtained in each case (no yields are quoted). He prepared dodeca-3,6-dione by electrolysing a mixture of 4,7-diketononanoic and valeric acids. Japanese investigators[202,324,325] obtained very satisfactory results in the electrolytic condensation, in methanol, of keto-acids with saturated acids and half-esters of dicarboxylic acids (40 A/dm^2, 30°–35°) (Table 11).

Good results have been obtained with keto-acids and substituted aliphatic acids. Thus, 4,7-diketooctanoic acid was condensed with 5-methoxyvaleric and β-isopentyloxybutyric acid[326]; the yield of 9-isopentyloxydeca-2,5-dione was 30%.

The number of possible "crossed" electrolytic-condensation reactions of acids with various substituents is very large. The methyl ester of 14-methoxy-3-methyltetradecanoic acid (34.4% yield) has, for instance, been prepared by the electrolysis, in methanol, of monomethyl β-methylglutarate and 11-methoxyundecanoic acid (Ni anode, Pt cathode, 5–7 A, 80–100 V)[326].

Hexadeca-2,15-dione (31% yield)[327] was synthesised by electrolysis, in anhydrous methanol, of acetylvaleric and acetylpelargonic acids (12.5 A/dm², 5 A, 50 V, 40°–50°).

The methyl ester of 10-acetamidodecanoic acid was obtained by electrolysing 6-acetamidohexanoic acid and monomethyl adipate[223,328].

No "crossed" products were obtained in the electrolysis of monomethyl adipate with acetylglycine and cyanoacetic acid (both substituted in the α-position to the carboxyl group)[223]. However, contrary to the general rule, Japanese investigators obtained satisfactory results in the simultaneous electrolytic condensation of methyldodecylcyanoacetic acid and lauric acid, ethyldodecylcyanoacetic acid and undecanoic acid[329], ethyldodecylcyanoacetic and capric acid, and also in the electrolysis of a mixture of the methyl ester of diisopentylmalonic acid and isocaproic acid[330]. (No reaction conditions or yields are given in these papers).

Hydrolysis of the products obtained in the electrolysis of monomethyl adipate with *threo*- and *erythro*-9,10-dihydroxystearic acid[171] in anhydrous methanol, using Pt electrodes, yielded *threo*- and *erythro*-13,14-dihydroxybehenic acid (24% and 33% yields, respectively). *Threo*-11,12-dihydroxy arachidic acid was prepared by an analogous method[124] from monobenzyl succinate and *threo*-9,10-dihydroxystearic acid (13% yield).

Mixtures of aliphatic-aromatic and mixtures of aliphatic-aromatic and aliphatic acids have also been subjected to "crossed" electrolytic condensation. In one of the early investigations[210] the diethyl ester of α-methylhydrocinnamic acid was found in the electrolysis products of a mixture of acetic acid and monoethyl benzylmalonate. t-Pentylbenzene (32% yield) was obtained by electrolysing 3-phenylisopentanoic acid in methanol, in the presence of an excess of sodium acetate (Pt anode, 15 A/dm², 60°)[271]. Electrolysis of palmitic with phenylacetic and β-phenylpropionic acids led to the formation of the corresponding hexadecyl- and heptadecylbenzene[175]. Electrolytic condensation of a mixture of γ-phenylbutyric acid with β-phenylpropionic or δ-phenylvaleric acids (Pt anode, 30°–40°) in a methanol-pyridine mixture (2 : 1)* gives, in the first case, small quantities of 1,5-diphenylpentane, and in the second 36% of 1,7-diphenylheptane[270].

"Crossed" condensation as well as the simple Kolbe condensation can be carried out in alcoholic, water–alcohol, or aqueous media. Under these conditions (especially in the last case) side reactions occurring concurrently with the electrolytic condensation, decrease appreciably the yield of the desired product.

Japanese chemists investigated the electrolytic-condensation reaction in water–alcohol solutions. They electrolysed palmitic and acetic, propionic and butyric, and stearic and acetic acids[322] in dilute alcohol at 70°–75°, using a Pt anode, and obtained the expected products (no yields are given). Electrolysis of the methyl ester of 2,12-dimethyltridecane-1,13-dicarboxylic acid with 6-methyldecanoic acid (Pt anode, 8 A/dm², pH 6.8–7, 30°) in 50% ethanol gave 3,13,19-trimethyltrieicosanoic acid (11% yield)[331,332] Under the same conditions the monoethyl ester of sebacic acid and 3,7-dimethyloctanoic acid[333] gave the ethyl ester of 11,15-dimethylhexadecanoic acid. Stearic acid (21% yield)[138] was isolated from the electrolysis products of the monomethyl ester of sebacic acid and decanoic acid when the process was effected in a 35% aqueous-methanol solution at a molar ration 1 : 3 of the initial components.

Electrolytic condensation of monoethyl adipate with some fatty acids in a water–alcohol solution[304] gave good results (Table 12).

Greaves et al.[138] compared results obtained in the "crossed" electrolytic condensation in alcohol and water–alcohol solutions. Hexanoic acid (40% yield) was obtained by condensing monomethyl adipate with acetic acid in anhydrous methanol (1.5–2 A, 40°–50°) whilst in a water–alcohol solution (3 A, 30°) the yield was only 29% (the molar ratio of the ester to acetic acid was in both cases 1 : 6). Decanoic acid was prepared by the electrolysis of a mixture of monomethyl adipate and hexanoic acid (1 : 1); in anhydrous methanol the yield was 36%, in a water–alcohol medium 12%. The same acid was synthesised in 50% yield by electrolysis of the monomethyl ester of sebacic acid in aqueous methanol in the presence of a large excess of acetic acid (molar ratio of the starting materials 1 : 15).

The "crossed" synthesis in aqueous solutions has been investigated even less than in water–alcohol solutions; there are practically no published data.

In 1895[334] the electrolytic condensation of monoethyl succinate with propionic, butyric, and isobutyric acids and of monoethyl malonate with acetic acid was carried out in an aqueous medium. The expected "crossed" products were obtained in each case.

Acetone[199] was prepared in 1900 by the electrolysis of an aqueous solution of potassium pyruvate and acetate in an electrolyser with a diaphragm (1.5–2 A, 17–18 V). The same author electrolysed in an aqueous medium (2.5 A and up to 20 V) mixtures of pyruvic and butyric acids, and also of levulinic and acetic or pyruvic acids, and obtained in the first two cases methyl propyl ketone, and in the last acetonylacetone.

The electrolysis of an aqueous solution of a mixture of the potassium salts of the monoethyl esters of malonic and suberic acids (1.7 A, 7.5 V, 15°) was carried out in 1922[134]. After saponification of the electrolysis products, succinic and dodecane-1,2-dicarboxylic acids were obtained, as well

TABLE 12.

Initial reactants		Solvent	"Crossed" product (after hydrolysis)	Yield, %
I	II			
$H_5C_2OOC(CH_2)_4COOH$	$C_5H_{11}COOH$	aqueous CH_3OH	$CH_3(CH_2)_8COOH$	23.3
»	$C_7H_{15}COOH$	»	$CH_3(CH_2)_{10}COOH$	15
»	$C_{15}H_{31}COOH$	aqueous C_2H_5OH	$CH_3(CH_2)_{16}COOH$	11.4
»	$(CH_3)_2CHCH_2COOH$	»	$(CH_3)_2CH(CH_2)_6COOH$	8

* Pyridine is added to inhibit the formation of polymers which coat the anode during electrolysis.

as the "crossed" product – azelaic acid. The yields are not quoted, probably because they were small. Only Miller and Hofer[334] were able to record good results in similar electrolytic-condensation reactions. For example, using small quantities of reactants, they prepared ethyl butyrate (69.5% yield) by the electrolysis of the potassium salt of acetic acid and the ethyl ester of succinic acid.

Samokhvalov et al.[336] stated in 1952 that 3–5% yields of the "crossed" product can be obtained by electrolysis of 11-methoxyundecanoic acid and of monoethyl β-methylglutarate.

Recent investigations[336,337] have shown that under certain conditions "crossed" electrolytic condensation can be successfully carried out in an aqueous medium. The electrolytic condensation of monoethyl adipate and 11-acetoxyundecanoic acid in an aqueous solution (24 A/dm², 40°–65°) can, after hydrolysis, give a 25–27% yield (based on 11-acetoxyundecanoic acid) of 15-hydroxypentadecanoic acid. Electrolysis of 11-hydroxyundecanoic acid and monoethyl adipate (molar ratio 1 : 3) gives a 7% yield of 15-hydroxypentadecanoic acid[336].

MECHANISM OF THE KOLBE REACTION

The mechanism of the Kolbe reaction is not entirely clear despite the large number of publications on the electrolytic condensation of carboxylic acids. The principal product and by-products have been investigated fairly thoroughly and in a large number of cases; several versions of the mechanism of transformation of the organic acids have been put forward. The nature of the anodic process, however – its kinetics, the role of the electrode surface in the condensation reaction, and the effect of the magnitude of the anode potential on the course of the reaction – have hitherto not been elucidated. In this respect, the electrolytic-condensation reaction does not appear to be an exception amongst other anodic processes including such apparently simple ones as, for example, the anodic evolution of oxygen from aqueous solutions.

Theories of the mechanism of electrolytic condensation developed in parallel with the extension of our knowledge of anodic processes and, in particular, of the evolution of oxygen.

In Kolbe's time it was assumed that only oxygen could be evolved at the anode during electrolysis of aqueous solutions; Kolbe, therefore, endeavoured to show that the electrolytic condensation was due to the oxidation of acids by oxygen, formed at the anode during the decomposition of water. The mechanism proposed by Kolbe was supported by several other investigators[43,338]. These hypotheses, as well as Bourgoin's[339,340] statement that anhydrides of the original acids are formed as intermediates in the Kolbe reaction, are only of historic interest.

In 1896 Schall[341] suggested that carboxylic acids are oxidised by the active oxygen liberated at the anode, and that diacyl peroxides are formed; decomposition of the latter would give the product of the Kolbe synthesis:

$$2RCOOH + O \rightarrow (RCOO)_2 + H_2O \qquad (RCOO)_2 \rightarrow R{-}R + 2CO_2.$$

Schall's hypothesis constituted the basis of Fichter's[33,342–345] peroxide theory of electrolytic condensation which found many supporters[105,346–348].

According to Brown and Walker's theory[5] the discharge of the carboxylic-acid anions and formation of uncharged radicals constitutes the primary process. The radicals can be condensed with simultaneous splitting off of carbon dioxide:

$$2RCOO^- \xrightarrow{-2e} 2[RCOO], \quad 2[RCOO] \rightarrow R{-}R + 2CO_2.$$

This was later developed as the free-radical theory[15,16,91,103,104,108–110,349].

Glasstone and Hickling's views, published in the 1930's[8,37,45,51,350–353], postulated that hydrogen peroxide, formed by discharge of OH^- ions at the anode, is the basic intermediate product; this idea was closely associated with the mechanism of electrolytic condensation. The authors also used the results of their detailed investigations on the electrolytic condensation of acetic acid and malonic-acid half-ester[6,37,45] in support of their theory, which is not, however, accepted by the majority of electrochemists at the present time.

The basic assumptions of the three theories of the electrolytic-condensation reaction are briefly discussed below.

The Peroxide Theory

This theory, proposed by Fichter in 1934[344], starts from the following scheme of electrolytic condensation:

$$2RCOO^- \xrightarrow{-2e} 2[RCOO] \rightarrow RCO{-}O{-}O{-}OCR \rightarrow 2[R] + 2CO_2\,; \quad 2[R] \rightarrow R{-}R$$

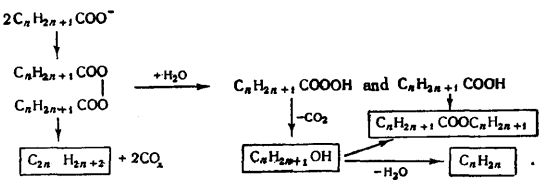
Unlike Schall, Fichter assumes that electrolytic condensation commences with the discharge of the carboxylic-acid anion, that diacyl peroxide is formed due to a further discharge of anions, and that the main product of the Kolbe synthesis is formed by the decomposition of the diacyl peroxide.

The formation of by-products is explained by the hydrolysis of the intermediate diacyl peroxide and the formation of the peracid which is converted to the alcohol by decarboxylation:

$$RCOO{-}OOCR + H_2O \rightarrow RCOOH + RCOOOH\,; \quad RCOOOH \rightarrow CO_2 + ROH.$$

In an alkaline medium and at low concentration of the initial anions, this decomposition of the peroxide is the principal reaction and alcohol is the principal product (Hofer–Moest reaction).

The alcohols can then be dehydrated to olefins (with the same number of carbon atoms), or react with the free acid, or the discharged anion, to form esters. Electrolytic condensation of saturated fatty acids can be represented as follows (according to the peroxide theory):



This scheme does not take into account the formation of saturated hydrocarbons C_nH_{2n+2}, which are usually obtained in significant quantities.

Many attempts have been made to prove the formation of the diacyl peroxide at the anode. Positive results were obtained only when electrolysis was carried out under special conditions, and the yields of peroxides were very small. Fichter et al.[129,354] succeeded in detecting diacyl peroxides and peracids during the electrolysis of caproate and the

half-ester of adipic acid, on strongly cooling the anode surface. Hallie[114], who carried out electrolysis experiments at low temperatures, using a circulating electrolyte, proved that small quantities of diacyl peroxides are formed during the electrolysis of acetates and caproates.

Many papers mention that the composition of the products of electrolytic condensation and of the chemical decomposition of diacyl peroxides is similar, which is regarded as a proof of the peroxide theory by its supporters. Diacetyl peroxide, for instance, decomposes on heating to form ethane, methane, and carbon dioxide[355-357].

A mixture of ethane and methane is formed when ultraviolet light acts on diacyl peroxides[357]. During the electrolysis of acetates, on the other hand, especially at low anodic current density, the formation of a mixture of ethane, methane, and carbon dioxide can also be observed[18,86,89,358].

Fichter suggests that the peroxide theory is also confirmed by the formation of glycolaldehyde during the electrolysis of acetate[33] and monoethyl malonate[7] in an ethylene-glycol solution. He regards the occurrence of the glycolaldehyde in both cases, as being due to the oxidation of ethylene glycol by the intermediate peroxides.

The Free-Radical Theory

This theory is the one most thoroughly developed at the present time and has many supporters.

During investigations on side reactions in the electrolytic condensation Hölemann and Clusius[103,104] carried out experiments on the electrolysis of deuterated acids dissolved in ordinary and in heavy water. They confirmed that a high current density is required in the electrolysis of acetates to produce ethane, and that a low current density (1 A/dm² and less) leads to the formation of methane. The deuterium content in the reaction products was proved to be determined solely by the composition of the acetate ion, not by the deuterium content of the water.

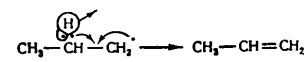
These results led the authors to the conclusion that the Kolbe reaction takes place via the formation of intermediate alkyl radicals – thus, in the electrolysis of acetates

$$CH_3COO^- \xrightarrow{-e} {}^{\cdot}CH_3COO\ ,$$
$${}^{\cdot}CH_3COO \rightarrow {}^{\cdot}CH_3 + CO_2\ .$$

Dimerisation takes place readily at high current density because the concentration of the methyl radicals at the anode is high; at low current density the methyl radicals can react with the acetate ions or with the molecules of the organic solvent (e.g. with alcohol if this is added to the electrolyte) and form methane.

$${}^{\cdot}CH_3 + {}^{\cdot}CH_3 \rightarrow C_2H_6\ ,$$
$${}^{\cdot}CH_3 + CH_3COO^- \rightarrow CH_4 + {}^{\cdot}CH_2COO^-\ ,$$
$${}^{\cdot}CH_3 + C_2H_5OH \rightarrow CH_4 + {}^{\cdot}C_2H_4OH\ .$$

By following the isotope composition of the products in the electrolysis of deuteropropionic[15,109] and deuterobutyric[110] acids, the authors concluded that unsaturated hydrocarbons (with half the number of carbon atoms of the main Kolbe-reaction products) are formed from the alkyl radicals, by the splitting off of the hydrogen atom originally in the β-position to the carboxyl group. The hydrogen atoms of the molecule itself do not migrate.



The formation of propane as well as propylene in the electrolysis of butyric acid is explained by the disproportionation of hydrogen in the alkyl radicals:

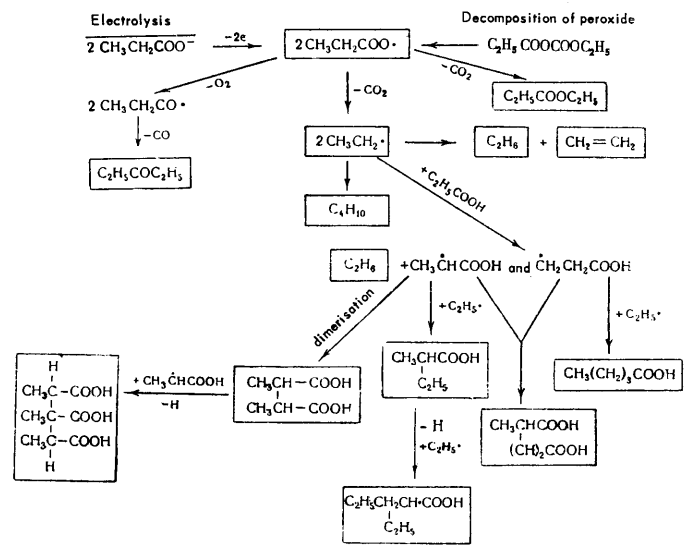
$$2CH_3{-}CH_2{-}CH_2 \rightarrow CH_3{-}CH_2{-}CH_3 + CH_3{-}CH{=}CH_2.$$

On electrolysis of an acid solution of α,α-dideuteropropionic acid (CH_3CD_2COOH), Kruis and Schanzer[15] obtained, among other products, a mixture of alcohols, containing 35% CH_3CD_2OH and 65% CD_2HCH_2OH, thus confirming that the oxidation of alkyl radicals to alcohols proceeds mainly at the β-position.

Goldschmidt and Stöckl[108] demonstrated the presence of free radicals during the electrolysis of fatty-acid salts by an indirect method, using the capacity of these radicals to initiate polymerisation of unsaturated compounds[359,360] (styrene, acrylonitrile). The formation of alkylpyridines when pyridine is present in the electrolyte is also regarded as an indirect proof of the presence of radicals[265,361].

Goldschmidt et al. made a detailed study of the composition of the electrolysis products of propionates in anhydrous propionic acid and compared them with the decomposition products of dipropionyl peroxide[16]. Later investigations dealt with the decomposition of symmetrical and unsymmetrical peroxides of dicarboxylic acids[362]. Goldschmidt stated that both the electrolysis of carboxylic acids and the decomposition of diacyl peroxides proceed via the formation of free radicals, but that the diacyl peroxides were not intermediate products in electrolysis.

The electrolysis of propionates and decomposition of dipropionyl peroxides, according to Goldschmidt, is shown in the following scheme:



The Glasstone–Hickling Theory

The theory[8,37,38,45,51,353] is based on the assumption that OH^- ions are discharged at the anode during the electrolysis

of aqueous solutions of fatty acids and form hydrogen peroxide; this reacts with the acid ions:

$$2RCOO^- + H_2O_2 \rightarrow R{-}R + 2CO_2 + 2OH^- .$$

The formation of radicals represents an intermediate stage:

$$2RCOO^- + H_2O_2 \rightarrow 2RCOO^{\cdot} + 2OH^-.$$

The latter may possibly combine and form diacyl peroxides – the intermediate products according to Fichter's theory:

$$2RCOO^{\cdot} \rightarrow [RCOO]_2.$$

When the concentration of hydrogen peroxide is not sufficiently high to effect the above reactions, or if the concentration of the anions is insufficient, hydrogen peroxide, or the active oxygen formed by its decomposition, will react with the acid and form the peracids:

$$RCOOH + H_2O_2 \rightarrow H_2O + RCOOOH \quad \text{or} \quad RCOOH + [O] \rightarrow RCOOOH.$$

The latter are decomposed to the alcohol and carbon dioxide:

$$RCOOOH \rightarrow ROH + CO_2.$$

Glasstone, Hickling, and Westwood carried out very detailed investigations on the electrolytic condensation of acetates [37,45] and monoethyl malonate [6] and endeavoured to correlate their results with the proposed mechanism, assuming the intermediate formation of hydrogen peroxide. The negative effect of the anode material (Ni, Fe, Au, etc.) and of foreign cations on the electrolytic condensation is related to their capacity to decompose hydrogen peroxide. The magnitude of the current density is related to the concentration of hydrogen peroxide set up in the layer close to the electrode. The effect of the pH of the medium on the yield of the main product is explained by the increased stability of hydrogen peroxide in acid solutions and by the decrease in the concentration of OH^- ions at lower pH.

Great importance is attached to the fact that the anode potential at which electrolytic condensation takes place is considerably higher than the potential at which oxygen is evolved from aqueous solutions. Hickling and Westwood [6] state that during the electrolysis of a 2 M solution of monoethyl malonate: (a) the potential is about 2.8 V on smooth platinum (when good yields of the diethyl succinate are obtained), and (b) on platinised platinum, gold, and lead dioxide the potential is approximately 2.0 V, in consequence of which no electrolytic condensation takes place. The polarisation curve for the evolution of oxygen in a phthalate buffer with identical pH was obtained for comparison. Oxygen was evolved when the anode potential was approximately 2.0 V.

Commenting on Hickling and Glasstone's work [45], Nekrasov pointed out that their assumption that "hydrogen peroxide, formed at the anode, gives rise to the formation of radicals which are capable of establishing a much higher potential than the potential of oxygen evolution" cannot be upheld, since changes in the anode surface and increases in oxygen overvoltage can occur, without any participation of hydrogen peroxide. Indeed, many publications [91,363] deny that the formation of hydrogen peroxide plays an indispensible part in anodic processes.

Glasstone and Hickling's proposed mechanism for the evolution of oxygen and other anodic processes is rejected by most electrochemists. All attempts to effect the Kolbe synthesis by the action of hydrogen peroxide on acetate solutions have proved unsuccessful [6,8,37]. The action of persulphates [6,37,343,364,365] and of fluorine [366,367], however, gives the same products as the electrolytic condensation.

Obviously, the electrochemical aspects of the Kolbe reaction can be elucidated completely only when much more is known about anodic processes, especially about the mechanism of oxygen overvoltage at the anode.

At present it can only be stated that the evolution of oxygen at a platinum anode proceeds in two stages: (a) interaction of an OH^- ion with the metal electrode, forming a higher platinum oxide; (b) decomposition of the higher oxide with formation of oxygen.

Some authors [368,369] assume that the discharge of OH^- ions is the slowest stage, determining the magnitude of the overvoltage. Others [370-373] attach great importance to the decomposition of the higher platinum oxides, the formation of which has been demonstrated in a number of investigations [371-373].

It can be assumed that the discharge of the carboxylic-acid ion and its simultaneous interaction with the higher platinum oxides (formed at the electrode) is a necessary condition for the electrolytic condensation.

The anomalously large anode potentials during the reaction, recorded by Glasstone and Hickling, are not surprising as the presence of carboxylic-acid ions, especially at high current densities, can increase the oxygen overvoltage to a considerable degree; this also occurs during the anodic evolution of oxygen from solutions containing SO_3^{2-} ions [372]. Apparently, under these conditions the discharge of $R\text{-}COO^-$ ions is energetically more probable than the discharge of hydroxyl ions, especially as the concentration of the latter is insignificant under conditions which are optimal for the electrolytic condensation.

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THE MECHANISM OF TRANSPORT OF MATTER IN POROUS SORBENTS

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INTRODUCTION

Porous sorbents are widely used in industry, both as adsorbents and as a matrix for various additives for absorption, chemisorption, and catalysis. In either case the effectiveness of the sorbent is primarily determined by its capacity and by the sorption velocity, both of which are appreciably dependent on the porous structure of the sorbent. The relationship between sorbent capacity and pore structure has been described in detail in many publications. The work of M. M. Dubinin and his collaborators, in particular, has helped to clarify this relationship. The structure-dependence of the adsorption velocity, on the other hand, has not been so fully investigated. It is nevertheless an important aspect of the technology of sorbents, since the development of a rational pore structure is impossible without a knowledge of the kinetic properties of the sorbent.

A sufficiently clear understanding of the mechanism of matter transport in the pores of a sorbent is a prerequisite to success in the search for the optimum sorbent porosity. This mechanism differs in many respects from that attending the transport of gases and liquids through layers of granular materials, such as soils, which has been considered in detail in a number of monographs[1-6]. For instance, when substances are adsorbed in the pores of a sorbent we notice special effects due to auxiliary modes of transport. Furthermore, the greater inhomogeneity of the pore structure of a sorbent, as compared with that of a layer of granular material, also plays an important part.

A considerable number of publications devoted to the mechanism of transport of gases adsorbed in the pores of sorbents has appeared during the past 10 years in the Russian and more especially in the foreign literature. It does not therefore seem out of place to present a review of the main contributions, preceded for the sake of completeness, by a discussion of the main modes of transport of non-adsorbed gases.

I. TRANSPORT OF NON-ADSORBED GASES

Viscous Flow

A pressure gradient in a porous body gives rise to a flow of gas in the direction of the gradient. The type of motion depends on the ratio of the mean free path of the molecules Λ to the capillary radius r. If $\Lambda/r \ll 1$ the gas flow is viscous; if on the other hand $\Lambda/r \gg 1$ molecular flow sets in. The first case is characterised by collisions of the gas molecules with one another; in the second case collisions between gas molecules and pore walls predominate. Viscous flow may be laminar or turbulent according to the value of the Reynolds number

$$\mathrm{Re} = \frac{wd}{\nu}, \qquad (1)$$

where w is the mean linear velocity of flow, d the pore diameter, and ν the kinematic viscosity.

In cylindrical pipes laminar flow is maintained[7] up to $\mathrm{Re} < 2200$. In granular layers the onset of turbulence takes place at considerably smaller Reynolds numbers because of the tortuous channels and of the periodic narrowing and widening of the pores. The transition from laminar to turbulent flow in this case has been reported by various authors[8-10] in the region $20 < \mathrm{Re} < 200$. Within the grains of sorbents laminar flow occurs[11] up to $\mathrm{Re} \leqslant 4-6$. Further criteria have been put forward, appropriate to the analysis of the motion of gas in porous bodies[12]. The flow of gas through sorbents as commonly used is laminar owing to the smallness of the pore radii.

Darcy's equation,

$$\frac{V}{t} = B \operatorname{grad} p, \qquad (2)$$

expresses the speed of laminar flow of incompressible liquids, and also of gases under conditions when the variations in density can be ignored (small pressure drop). In Eqn. (2) V is the volume of liquid or gas in cm^3, p the pressure in bars, t the time in sec, and B a constant expressing the permeability of the porous medium.

For a single cylindrical capillary, as shown by Hagen[14] and Poiseuille[15]

$$B = \frac{\pi r^4}{8\eta}, \qquad (3)$$

so that the speed of flow of gas is given in this case by

$$\frac{V}{t} = \frac{\pi r^4}{8\eta} \frac{p_1 - p_2}{l}. \qquad (4)$$

In Eqns. (3) and (4) r is the capillary radius, η the gas viscosity, p_1 and p_2 the pressures at the ends of the capillary, and l the length of the capillary.

When the change in density of the gas within the capillary cannot be ignored, Eqn. (4) is modified to

$$\frac{pV}{t} = \frac{\pi r^4}{8\eta} \bar{p} \frac{\Delta p}{l}, \qquad (5)$$

where p is the pressure under which the volume of the effluent gas is measured, $\bar{p} = \frac{p_1 + p_2}{2}$ is the mean pressure, and $\Delta p = p_1 - p_2$.

The permeability of various bodies may be compared on the basis of the speed of flow under a pressure difference of 1 bar,

$$K = \frac{pV}{t\Delta p} = \frac{\pi r^4}{8\eta} \bar{p} \frac{1}{l}. \qquad (6)$$

The permeability K, when referred to unit cross-section and unit length of sample, is called the specific permeability K_0:

$$K_0 = \frac{K}{F} l. \qquad (7)$$

The specific permeability of a capillary of circular cross-section for compressible gases is given by*

$$K_0 = \frac{r^2}{8\eta} \bar{p}, \qquad (8)$$

* Barrer[16] omits the mean pressure $\bar{p}$ in the expression for K_0.

whereas that of a capillary with a cross-section of arbitrary shape is given by

$$K_0 = \frac{r_m^2}{k\tau_i}\bar{p}, \qquad (9)$$

where $r_m = \frac{F}{P}$ is the hydraulic radius, F the cross-sectional area, P the perimeter, and k a coefficient determined by the shape of the cross-section of the capillary.

Values of k corresponding to various cross-sectional shapes[17] are given in Table 1.

It can be seen from Eqn. (8) that the permeability to viscous flow decreases sharply as the capillary radius is decreased.

Viscous flow takes place, as pointed out above, for $\Lambda/r \ll 1$. The pores of sorbents range, in dimensions, from those visible with a magnifying glass to those of molecular size. In the coarser pores (radius $r = 10^{-2}-10^{-3}$ cm) viscous flow is possible only for gas pressures not less than 1 mm Hg. The mean free path at atmospheric pressure equals 10^{-5} cm approximately, so that viscous flow under these conditions is observed only in pores with $r > 10^{-5}$ cm. In the finest pores ($r = 10^{-7}-10^{-6}$ cm) viscous flow under atmospheric pressure is impossible.

TABLE 1. Value of k of Eqn. (9).

Shape of capillary cross-section		k
Circle		2
Square		1.78
Rectangle: height / width	h	
	$b=2h$	1.94
	$b=5h$	2.38
	$b=10h$	2.65
Parallel surfaces (fissure)		3.0
Ellipse: semi-axes a and b		
	$a=2b$	2.13
	$a=10b$	2.45

TABLE 2. Factor b for different values of l/r.

$\frac{l}{r}$	0	0,2	0,5	1,0	1,5	2,0	3	5	10	20	50	100	1000	∞
b	1	0,909	0.801	0.672	0.581	0.514	0.421	0.315	0,197	0.114	0.050	0,026	0,0027	$\frac{8r}{3l}$

Molecular Diffusion

At very low gas pressures, or with capillaries of very small radius, the mean free path of the molecules becomes much larger than the capillary radius, and the collisions between the gas molecules and the capillary wall greatly exceed those between the molecules themselves. The molecules colliding with the wall rebound in all directions, and only a small fraction is reflected specularly.

A diffuse reflection of this kind can be due to two causes: (1) no surface is truly flat on a microscopic scale; projections and cavities can be expected to reflect impinging molecules in all directions; (2) all substances are adsorbed to a greater or lesser degree, so that molecules must exist in the adsorbed condition for a certain time after collision; their eventual re-emission results from thermal vibrations and is equally probable in all directions.

Molecular diffusion in capillaries was first investigated by Knudsen[18], who showed that the speed of steady-state molecular diffusion in straight capillaries of circular cross-section is satisfactorily expressed by

$$\frac{pV}{t} = \frac{4\pi r^3}{3}\sqrt{\frac{2RT}{\pi M}}\,\frac{\Delta p}{l}, \qquad (10)$$

where M is the molecular weight of the gas, T the absolute temperature, and R the gas content.

By analogy with Eqn. (8) the specific permeability of a capillary to molecular diffusion can be written

$$K_M = \frac{4r}{3}\sqrt{\frac{2RT}{\pi M}}. \qquad (11)$$

It follows from Eqn. (11) that the permeability of a capillary to molecular diffusion is independent of the gas pressure.

Formula (10) applies to a straight capillary of circular cross-section on the assumption that all colliding molecules are reflected according to the cosine law, that $r/\Lambda = 0$, and $l/r = \infty$. Certain corrections must be introduced when these conditions are not met.

Allowance for specular reflection. If f is the fraction of diffuse reflections and $1 - f$ the fraction of specular reflections, Knudsen's formula becomes

$$\frac{pV}{t} = \frac{4\pi r^3}{3}\sqrt{\frac{2RT}{\pi M}}\,\frac{\Delta p}{l}\,\frac{2-f}{f}. \qquad (12)$$

In many cases of practical importance the value of f approaches unity.

Correction for finite capillary length. Clausing[19] proposed the following formula for the permeability of capillaries of finite length with $l/r < 1000$:

$$\frac{K_l}{l} = b\sqrt{\frac{RT}{2\pi M}}, \qquad (13)$$

where K_l is the specific permeability of a capillary of length l, and b the probability that a molecule will pass through the capillary without being turned back. Values of the Clausing factor are listed in Table 2.

From Eqns. (11) and (13) we find that

$$\frac{K_l}{K_M} = \frac{3}{8}\,b\,\frac{l}{r}. \qquad (14)$$

The ratio K_l/K_M, calculated from Eqn. (14) for several values of l/r, is tabulated in Table 3.

TABLE 3. Ratio K_l/K_M for different values of l/r.

l/r	0,5	1	2	3	5	10	100	1000
K_l/K_M	0,152	0.252	0.384	0,474	0.588	0.737	0,972	0.998

It follows from the data of Table 3 that the values of K_M calculated from formula (11) for capillaries with a small ratio l/r are much too high. Pollard and Present[20] give a detailed discussion of the permeability of short capillaries in the Knudsen region.

Allowance for capillary convolutions. Knudsen's formula (10) is derived for a straight capillary, but the capillaries of porous bodies are far from straight.

Hiby and Pahl[21-24] suggest that tortuous capillaries can be described as a series of straight capillaries for which $2 < l/r < 10$. In the case of systems with a globular structure, the authors replace the channels between the particles by a system of curved capillaries with $l/r = 3$. This lowers the permeability by approximately a factor of 2 (see Table 3) as compared with the straight-capillary model.

Permeability of non-cylindrical capillaries. The specific permeability of capillaries with an arbitrary cross-sectional shape is given[25] by the equation

$$K_M = \frac{8F}{3P}\sqrt{\frac{2RT}{\pi M}}, \qquad (15)$$

where F is the cross-section and P the perimeter of the capillary.

Gas Flow in the Transition Region

A decreased permeability is observed in the transition region (i.e. when the mean free path is approximately equal to the diameter of the capillary). The curve of K vs. $\bar{p}$ shows a minimum, in the region where $r/\Lambda = 0.2-0.3$, whose depth amounts to about 5% of the permeability for molecular diffusion. An example of this behaviour is given in Fig. 1, based on some measurements by Knudsen[18] of the permeability of glass capillaries to carbon dioxide. Similar results have been obtained by Close[26,27], Adzumi[28], Clausing[19], and others. Much effort has been directed towards explaining[29-34] the nature of the minimum in the permeability curve, but the phenomenon is still far from clear.

It follows from Eqn. (6) that the permeability to viscous flow should decrease linearly with pressure down to $p = 0$. In the low pressure region, however, the viscosity coefficient does not remain constant and independent of pressure, as required by Maxwell's molecular-kinetic theory[35], but decreases with pressure.

Meyer[36], who observed a decrease in the viscosity of air at low pressures, invoked gas slip in the neighbourhood of the solid surface to explain the result. He suggested that the coefficient of slip is related to the mean free path by the expression

$$\zeta = \frac{2}{3}\Lambda, \qquad (16)$$

which becomes

$$\zeta = \frac{2}{3}\Lambda\left(\frac{2}{f} - 1\right) \qquad (17)$$

if some of the molecules undergo specular reflection.

The first experimental determination of ζ is due to Kundt and Warburg[37-39]. These authors found a slip coefficient for air, normalised to $p = 760$ mm Hg, of $\zeta = 0.79 \times 10^{-5}$. Millikan[40] obtained $\zeta = 0.77 \times 10^{-5}$ for air and oil by the falling drop method. Further experimental methods for determining ζ are given by Stacy[41], and Skillman and Van Dyke[42].

Kundt and Warburg expressed the Hagen–Poiseuille equation, corrected for slip, in the form

$$\frac{pV}{t} = \frac{\pi r^4}{8\eta}\,\bar{p}\,\frac{\Delta p}{l}\left(1 + 4\frac{\zeta}{r}\right). \qquad (18)$$

The equation correctly predicts that the slip correction is considerable in the low pressure region, and that the speed of flow accordingly increases. At very low pressures, when molecular flow sets in, Eqn. (18) is obviously inapplicable.

Knudsen's semi-empirical equation satisfactorily describes the velocity of gas transfer over a wide range of pressures, embracing both viscous flow and molecular diffusion:

$$\frac{pV}{t} = \left(\frac{\pi r^4}{8\eta}\bar{p} + \frac{1 + c_1 p}{1 + c_2 p}\cdot\frac{4\pi r^3}{3}\sqrt{\frac{RT}{\pi M}}\right)\frac{\Delta p}{l}, \qquad (19)$$

where

$$c_1 = 2.00\frac{r}{\eta}\sqrt{\frac{\rho}{p}},$$

$$c_2 = 2.47\frac{r}{\eta}\sqrt{\frac{\rho}{p}},$$

and ρ is the density of the gas.

According to Wicke[34] both types of transport (laminar flow and molecular diffusion) take place in a sufficiently long capillary; as the pressure continuously drops along the length of the capillary, it is possible for the flow to become molecular. Wicke obtained a formula analogous to Eqn. (19) by considering the flow in the transition region as two currents in series (viscous and molecular).

Porous sorbents contain channels of every conceivable size and therefore support the transitional mode of flow over a wide range of pressures.

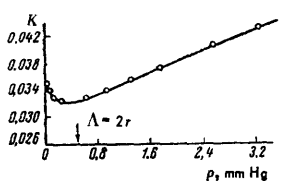


Fig. 1. Permeability of a glass capillary to carbon dioxide, after Knudsen[18].

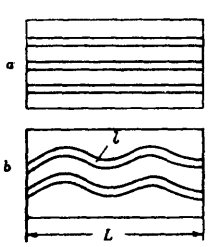


Fig. 2. Simplest model of a porous medium. $l = K_1 L$.

Model of a Porous Body. Mixed Transport

The questions discussed above relate to the flow of gas in a single capillary. Sorbents, with their multitude of pores of different sizes and arbitrary cross-sections, variously interconnected, present a much more complicated picture. Quantitative discussions of the process of matter transport in real porous bodies must therefore rely on some simplified model of the sorbent structure.

Leibenzon, in his study of the permeation of gas through soils[1], used as preliminary models of the porous system a bundle of straight, cylindrical, parallel capillaries of uniform radius ("ideal soil") or a layer of spherical particles of uniform size ("fictitious soil"). The "ideal soil" concept (Fig. 2) was applied to studies of the sorption process by Damköhler[43], Barrer[44], Flood[45], Dacey[46], and others. One of the deficiencies of this model is the fact that its transverse permeability, unlike that of an actual system, is zero.

Adzumi[48] modified the "ideal-soil" model by assuming a system of cylindrical, parallel capillaries of non-uniform diameter. Each capillary consists of a series of capillaries of different lengths and diameters, joined end-to-end. Adzumi's model of a porous body is shown schematically in Fig. 3.

Wicke[49,50] and Dubinin[51], in their studies of sorption by active carbons, assumed a pore structure consisting of branching chains of coarse pores, freely interconnected. Micropores are taken to be ramifications of the coarse pores, as shown in Fig. 4.

Wiggs assumes that zones of high and of low conductivity are present in the particles of sorbents[52]. Their relative extent, and mutual disposition, depend on the preparative conditions, and may vary. A schematic view of Wiggs' model is given in Fig. 5.

A globular structure characterises silica gel[53-55]. Obviously, the "fictitious soil" model is more suitable in this case.

Deryagin and Bakanov's theoretical study[33] of the flow of gas in the transition region is based on a model of a highly-porous medium consisting of a system of randomly distributed spheres, rigidly fixed but not in contact with each other.

Sorbent particles may contain fissures due to the shrinkage and disintegration of the material during preparation, or embody elements of the structure of the parent material, as is the case with wood charcoals[56]. This makes the structure of real sorbents even more complicated; a quantitative calculation of the influence of such structural features on the kinetics of the sorption process is exceedingly difficult.

On the basis of simple considerations, Adzumi derived an expression of the following form for the permeability of his model of a porous medium:

$$K = \frac{\pi}{8\eta}\bar{p}\sum^{n}\frac{1}{\sum^{m}\frac{l}{r^4}} + \gamma\frac{4\pi}{3}\sqrt{\frac{2RT}{\pi M}}\sum^{n}\frac{1}{\sum^{m}\frac{l}{r^3}}, \qquad (20)$$

where n is the number of capillaries connected in parallel, m the number connected in series, and γ is a constant.

In the case of sorbents with pores of a single kind both the effective pore radius and the number of pores per unit area of sample can be calculated from Eqn.(20). Assuming

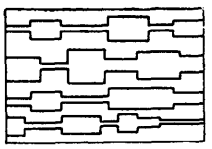


Fig. 3. Azumi's model of a porous medium[48].

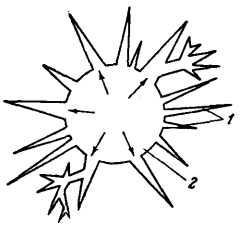


Fig. 4. Network of transport pores and adsorption pores, after Wicke[49,50]. 1) adsorption pores; 2) transport pores.

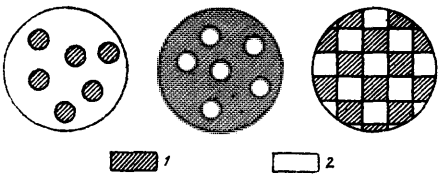


Fig. 5. Pore structure of a sorbent, after Wiggs[52]: 1) poorly conducting regions; 2) highly conducting regions.

uniform pores of length l and radius r, the equation can be written

$$K = A_0\bar{p} + \gamma B_0, \qquad (21)$$

where $A_0 = \frac{\pi r^4}{8\eta l}n$ and $B_0 = \frac{4\pi}{3}\sqrt{\frac{2RT}{\pi M}}\frac{r^3}{l}n$.

The quantities A_0 and B_0 can easily be obtained from a study of the variation of K with pressure $\bar{p}$. Assuming $\gamma \cong 1$, we have

$$r = \frac{A_0}{B_0} \text{ and } n = \frac{B_0^4}{A_0^3}.$$

The surface area of the pores (S) can then be derived from the value of r by means of the formula

$$S = \frac{2\epsilon}{r}, \qquad (22)$$

where ϵ is the relative pore volume in cm^3/cm^3.

The determination of the specific area of powders is based on considerations similar to the above[57-75]. The method has been critically appraised, and its limitations

discussed, in a number of papers. The whole problem has been re-examined quite recently[76].

The K - $\bar{p}$ curves for porous media frequently show no minimum[32]. According to Pollard and Present[20], this is due to a large number of short capillaries ($l < 2\Lambda$), whose permeability is less than that calculated from Knudsen's formula. Consequently, the limit of K for $p = 0$ is in fact lower than usually supposed. As shown theoretically by Deryagin and Bakanov[33], the K - $\bar{p}$ curve for highly porous bodies (porosity $\epsilon > 0.7$) must have a minimum.

Dacey and Fendley[46] report that the adsorption of argon and of methane, in quantities greater than 5% by weight, alters the pore structure of saran charcoal. The flow of helium in a given pressure region, which was molecular before the adsorption of argon, became viscous after argon adsorption. No such effects were noticed with argon adsorptions less than 3%.

When the sorbent pores are initially filled with some foreign gas, e.g. air, and no pressure gradient exists, the transport of another gas depends on volume diffusion in the pores, a case of frequent practical occurrence. The diffusion will be of the common, or of the Knudsen type, according to the value of the ratio Λ/r. The diffusion equations, and their solution for various geometries, are discussed in a number of monographs[77-79].

II. TRANSPORT OF ADSORBED GASES

The concept of adsorbed and non-adsorbed gases is somewhat arbitrary. We know that all gases and vapours are adsorbed on solid surfaces to a greater or lesser extent. From this point of view, non-adsorbed gases do not exist. The adsorbability of a given substance depends on the conditions under which the adsorption proceeds. Nitrogen, for instance, is hardly adsorbed at ordinary temperatures, but its adsorption at low temperatures may be considerable. We will define a non-adsorbed gas as one whose adsorption under the relevant conditions is so small as not to affect significantly the speed of flow through the porous medium.

The permeability of porous bodies to non-adsorbed gases is most frequently described using Adzumi's equation:

$$K = \frac{A}{\eta}\bar{p} + B\sqrt{\frac{T}{M}}, \qquad (23)$$

where A and B are structural parameters, related to the size, number, and shape of the pores.

Good agreement between calculation and experiment is usually obtained when the constants A and B, derived from experiments on one non-adsorbed gas, are used to predict the flow characteristics of another non-adsorbed gas. However, if the same procedure is applied to adsorbed gases the calculated values are invariably low. These observations are reported by many independent workers[31,80-86].

Several hypotheses have been advanced to explain the increased speed of flow of adsorbed gases. The most prevalent invokes a subsidiary flow of matter in the adsorbed phase, by means of molecular migration along the surface. This point of view is developed in the papers of Barrer, Carman, Haul, and others[87-92].

Tomlinson and Flood[31] consider that the greater permeability to adsorbed gases is a manifestation of the importance of slip, since the density of these gases is considerably increased near the pore walls. In more recent publications[93-99] Flood has developed the idea of a flow of matter in the adsorbed phase. The overall flow of gas in the porous medium is increased by this auxiliary transport mechanism.

Diffusion Along the Sorbent Surface

Molecules adsorbed on the surface of solids are in a state of continuous thermal motion, and are able to migrate along the surface under the influence of a concentration gradient. The first demonstration of this phenomenon is due to Vollmer and Esterman[100] who studied the growth of mercury crystals at -63° from the vapour of mercury at -10°. They observed an extremely rapid growth of thin hexagonal crystals in the direction of the hexahedral plane. The linear crystallisation velocity was about 1000 times greater than could be accounted for by the molecular-kinetic theory. Later work by Vollmer, and also by other authors, considers surface migration in different systems[101-107]. Various methods have been applied to the study of the mobility of adsorbed molecules[108-114], notably the adsorption method, which is based on the evaluation of the adsorption entropy.

Clausing[115] and Damköhler[43] were the first to attempt an appraisal of the surface-migration effect in relation to the velocity of transport of adsorbed gases in capillaries. These workers expressed the diffusion current P in the direction of the concentration gradient as the sum of two parallel flows: one in the gas phase (P_g) and one along the surface (P_a). In the steady state the rate of mass transport is proportional to the concentration gradient, i.e.:

$$P = P_g + P_a = -\left(D_g\frac{\partial c}{\partial x} + D_a\frac{\partial a}{\partial x}\right), \qquad (24)$$

where D_g and D_a are the diffusion coefficients appropriate to the gaseous and to the adsorbed phases respectively; $\frac{\partial c}{\partial x}$ is the concentration gradient in the gas phase; $\frac{\partial a}{\partial x}$ is the concentration gradient in the adsorbed phase.

Assuming a linear adsorption isotherm $a = Hc$ (where H is Henry's constant) we can writen Eqn. (24) as

$$P = -\left(D_g\frac{\partial c}{\partial x} + D_a H\frac{\partial c}{\partial x}\right) \qquad (25)$$

or

$$P = -D_g\left(1 + \frac{D_a H}{D_g}\right)\frac{\partial c}{\partial x}. \qquad (26)$$

For non-stationary one-dimensional diffusion we have the analogous equation

$$\frac{\partial c}{\partial t} + \frac{\partial a}{\partial t} = D_g\frac{\partial^2 c}{\partial x^2} + D_a\frac{\partial^2 a}{\partial x^2}, \qquad (27)$$

which in the case of a linear adsorption isotherm takes the form

$$\frac{\partial c}{\partial t} = \frac{D_g + D_a H}{1 + H}\frac{\partial^2 c}{\partial x^2}. \qquad (28)$$

In the majority of cases $H \gg 1$, so that

$$\frac{\partial c}{\partial t} = D_e\frac{\partial^2 c}{\partial x^2}, \qquad (29)$$

TABLE 4. Diffusion coefficients D_a and D_g in carbon cylinders.

Gas	ε=0.37		ε=0.64	
	$D_a \times 10^5$	$D_g \times 10^5$	$D_a \times 10^5$	$D_g \times 10^5$
He	1.74	5.7	2.7	15.4
Ne	1.05	2.6	1.6	6.7
H_2	2.8	8.3	4.2	20.9
A	0.16	1.9	0.54	4.7
N_2	0.21	2.2	0.61	5.6
Kr	0.05	1.2	0.13	3.1

TABLE 5. Values of D_a and D_g on porous glass.

Gas	$D_a \times 10^5$	$D_g \times 10^5$
O_2	2.05	8.8
N_2	2.26	9.4
A	1.91	7.9
Kr	0.78	5.4
CH_4	0.73	12.4
C_3H_6	0.60	9.0

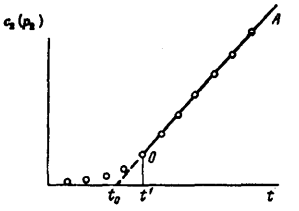


Fig. 6. Determination of the 'time-lag'.

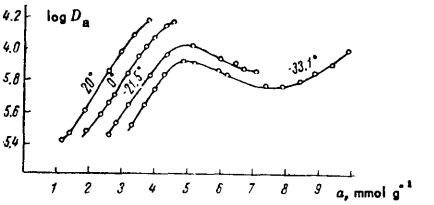


Fig. 7. Variation of the coefficient of surface diffusion with amount adsorbed, after Carman and Raal[84] (freon on compacted soot). The ordinates should be read with a minus sign.

where $D_e = \frac{D_g}{H}\left(1 + \frac{D_a H}{D_g}\right)$ is the effective diffusion coefficient.

In both cases (26) and (28) the migrational effect is estimated from the value of the expression $\frac{D_a H}{D_g}$.

If $\frac{D_a H}{D_g} \ll 1$, the fraction transported in the adsorbed phase is small and the contribution of surface diffusion to the rate of transport can be ignored. If, on the other hand, $\frac{D_a H}{D_g} \gg 1$, surface diffusion dominates the process of matter transport. Many other authors have also adopted a similar method for evaluating the part played by surface diffusion in the transport process.

Damköhler computed the expression $\frac{D_a H}{D_g}$ as follows. We know, from the molecular-kinetic theory, that $D_g = 1/3\, u\Lambda$. Assuming a mean pore radius $r = 10^{-6}$ cm for active carbon, and an average molecular velocity $u = 3 \times 10^4$ cm sec^{-1}, he obtained a diffusion coefficient for the gas phase of $D_g = \frac{2ru}{3} = 2 \times 10^{-2}$ cm^2 sec^{-1}. By treating the adsorbate as a two-dimensional gas, for which $D_a = 1/2\, u_a \Lambda_a$ (where u_a and Λ_a are the mean velocity and the mean free path of the molecules in the adsorbed layer), and assuming that $u_a = 3 \times 10^4$ cm sec^{-1} and $\Lambda_a = 4 \times 10^{-8}$ cm, Damköhler obtained $D_a = 6 \times 10^{-4}$ cm^2 sec^{-1} for the coefficient of surface diffusion. For readily adsorbed materials Henry's constant is of the order of 10^3, whence the expression $\frac{D_a H}{D_g} \cong 30$, i.e. is considerably in excess of unity. On the strength of these considerations Damköhler concludes that the transport of readily adsorbed substances is dominated by surface diffusion. Clausing's evaluation[115,116] of the migrational effect led him to similar conclusions. He showed that surface diffusion could be ignored for the case of argon on glass. Taking $\Lambda_a = 30 \times 10^{-8}$ and a capillary radius $r = 0.005$ cm, he finds $\frac{D_a H}{D_g} \ll 1$.

Later publications attempt more direct assessments of the role of surface diffusion. They follow three distinct approaches: (1) determination of the coefficient of surface diffusion from the experimental values of the overall ($D_0 = D_g + D_a H$) or of the effective (D_e) diffusion coefficient, and of the gas-phase diffusion coefficient (D_g); (2) comparison of the activation energy of the inner diffusion process with the heat of adsorption; and (3) total or partial elimination of the volume-diffusion component of the transport process.

The overall diffusion coefficient is most frequently determined by permeability measurements under steady-state conditions.

The method is essentially the following. Gas concentrations c_1 and c_2 (or pressures p_1 and p_2), constant with time, are maintained on the two sides of a porous slab of thickness L. After a time, a steady-state flow is set up, and its speed is determined by the equation

$$P = KF\frac{p_1 - p_2}{L}. \qquad (30)$$

In the absence of viscous flow, i.e. if the flow is molecular, or if a carrier gas is present, the constant K is related to the overall diffusion coefficient by the expression

$$K = D_0 \varepsilon. \qquad (31)$$

Making use of Eqn. (26), the overall diffusion coefficient becomes

$$D_0 = D_g\left(1 + \frac{D_a H}{D_g}\right). \quad (32)$$

For non-adsorbed gases

$$\frac{D_a H}{D_g} = 0 \text{ and } K = D_g\varepsilon. \quad (33)$$

Experiments with adsorbed and non-adsorbed gases yield K, whence D_0 and D_g are calculated by means of Eqns. (31) and (33). D_a is then derived from Eqn. (32). It remains understood that this calculation can only be meaningful if the assumption of a linear adsorption isotherm, upon which Eqn. (32) is based, is justifiable.

The "time-lag" method is widely used for determining the effective diffusion coefficient $D_e = D_0/H$. It consists of the following. On one side of the porous slab we maintain a constant gas concentration c_1, and on the other side $c_2 \cong 0$. Under these conditions the flow through the slab will be as shown in Fig. 6. If the diffusion is allowed to take place into a closed volume we find that from a time t' onwards the concentration c_2 in this volume increases linearly with time provided that c_2 remains, throughout, much smaller than c_1. Diffusion is now proceeding under stationary conditions. The intercept obtained on the t axis by producing the line OA gives the time t_0, corresponding to $c_2 = 0$, and related to the effective diffusion coefficient by the expression

$$t_0 = \frac{k_1^2 L^2}{6D_e}, \quad (34)$$

where L is the thickness of the porous slab and k_1 is a coefficient which allows for the sinuosity of the channels (see Fig. 2*b*).

Eqn. (34) is an approximate solution of the differential equation for diffusion, obtained[88] for the boundary and the initial conditions stated above. Deryagin[117] gives a statistical derivation of Eqn. (34).

Some doubt exists as to the value of k_1 for porous bodies. For granular layers[47,57,118] $k_1 = 1.4 - 2.0$, but anomalously high values have been obtained in the case of porous substances[119] by electrical conductivity and other methods. Fortunately, k_1 can be eliminated from relative calculations involving adsorbed and non-adsorbed gases.

The possible use of the time-lag method of determining the effective diffusion coefficient in cases where the diffusion "constant" is a function of concentration has been examined[120]. Methods for deriving D_e from measurements of the rates of adsorption from a constant volume but under different gas concentrations are discussed by Carman and Haul[121].

Barrer and Strachan's[92] values for D_a and D_g, obtained by the time-lag method, are listed in Table 4. In this interesting investigation the authors studied the permeability of cylinders of soot, compacted under various pressures. The porosity ϵ of these carbon cylinders varied from 0.37 to 0.79. The mean pore sizes, estimated by the authors for specimens of porosity 0.37 and 0.64, were 6.5 and 18.8 Å respectively.

The same authors, assessing the migrational effect from the value of $\frac{D_a H}{D_g}$, came to the conclusion that the more readily adsorbed gases, such as nitrogen and krypton, are transferred mainly by surface diffusion.

Barrer and Barrie[44] have determined isotherms and sorption rates for a number of gases on porous glass. The Kelvin radius of the pores, estimated by formula (20) from measurements with different gases, was approximately 30 Å. Values of D_a and D_g, derived from experiments at 70°, are given in Table 5. Henry's constant varied from 2 to 8, and the value of the expression $\frac{D_a H}{D_g}$ was considerably less than one. These data led the authors to the conclusion that volume diffusion is the more important if the pore radius $r \geqslant 30$ Å.

Wicke and Kallenbach[87] investigated the permeability of carbon membranes to carbon dioxide, over the temperature range 0°–300°, by the stationary diffusion method. They found that the rate of penetration of carbon dioxide is considerably more dependent on temperature than should be the case for volume diffusion. Hence, they estimate that the contribution of surface diffusion to the transport process varies from 0 to 50% according to the conditions of their experiments.

The value of $\frac{D_a H}{D_g}$ increases with H if D_a is not a function of concentration. In the case of convex adsorption isotherms we can evaluate the contribution of surface diffusion over different regions of the isotherm by applying, for example, Carman's "differential method"[121]. The result is that in the region of low coverage this contribution is much smaller than that calculated on the assumption that the value of D_a, found at higher adsorptions, applies. It follows that the surface-diffusion coefficient decreases as the extent of adsorption decreases.

The variation of the surface-diffusion coefficient with extent of adsorption has been studied by a number of workers[83,84].

Fig. 7 shows the dependence of D_a on coverage, after Carman and Raal[84].

From a study of the permeability of paper to water vapour at various relative pressures, Vollmer[85] derived a linear relationship between the surface-diffusion flow and the product of the amount of adsorption, a, and the slope, $\Delta a/\Delta p$:

$$P_a = 2\pi r D_a a \frac{\Delta a}{\Delta p}. \quad (35)$$

Babbit[122] obtained a similar expression. Kammermeyer[123] gives a more precise form of Eqn. (35) by assuming that the diffusion current along the surface is described by

$$P_a = 2\pi r D_a\left[a_1\left(\frac{\Delta a}{\Delta p}\right)_1 - a_2\left(\frac{\Delta a}{\Delta p}\right)_2\right], \quad (36)$$

where a_1 and a_2 are the amounts of adsorption corresponding to pressures p_1 and p_2.

Activation Energy of the Diffusion Process in Porous Bodies

Dacey and Thomas[124-126] made a systematic attempt to evaluate the role of surface diffusion from the magnitude of the activation energy attending the inner-diffusion process. They proceeded from the hypothesis that diffusion must take place in the volume of the pores in those cases where the activation energy equals the heat of adsorption. Each jump of a molecule then results in its complete detachment from the surface. If, on the other hand, the observed activation energy is smaller than the heat of adsorption, the molecules

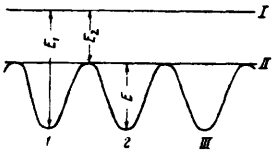


Fig. 8. Potential energy curve for a homogeneous adsorbent: I) energy of the gas molecules in the free volume; II) energy of the two-dimensional gas; III) energy of the adsorbed molecules.

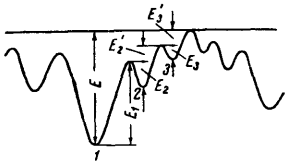


Fig. 9. Potential energy curve for an inhomogeneous adsorbent.

only slide about the surface. As we shall see below, this treatment is not entirely correct.

Molecular movements along the surface have activation requirements even in the case of homogeneous adsorbents with a regular crystal lattice. The heat of adsorption is the same for every site, but the transfer of adsorbate from position 1 to position 2 (see Fig. 8) nevertheless requires an activation energy given by

$$E = E_1 - E_2, \tag{37}$$

where E_1 is the energy of the adsorbed molecules and E_2 the energy of the two-dimensional gas.

The surface of real adsorbents is energetically even more heterogeneous. The potential energy curve for an inhomogeneous adsorbent is sketched in Fig. 9. The probability of a transition from position 1 to position 2 (Fig. 9) is given by $\nu e^{-E_1/kt}$, where ν is the vibration frequency of the adsorbed molecules. From position 2 the molecule can either revert to its original position 1 or go over to position 3. The probability of a transition from 2 to 3 is

$$\frac{1}{2}\exp\left[-\frac{E_2+E_2'}{kT}\right],$$

so that the combined probability for the complete transition from 1 to 3 will be

$$\frac{1}{2}\nu\exp\left[-\frac{E_1+E_2+E_2'}{kT}\right].$$

By carrying the argument further we can derive the probability of a transition in the presence of n energy barriers:

$$\left(\frac{1}{2}\right)^n \nu\exp\left[-\frac{E}{kT}\right]\exp\left[-\sum_{i=2}^{n}\frac{E_i}{kT}\right]. \tag{38}$$

If the quantity ΣE_i is sufficiently large, the probability that a molecule shall leave a given neighbourhood becomes small[127,128]. Hence it follows that (a) surface mobility, as inferred, for example, from the value of the adsorption entropy, does not necessarily imply free migration along the whole surface and ability to contribute to matter transport, and (b) the activation energy may be equal to the heat of adsorption even in cases of surface diffusion.

Frenkel'[129] relates the surface-diffusion coefficient to the mean time of residence in the adsorbed state:

$$D_a = \frac{\Delta}{4\tau}, \tag{39}$$

where Δ is the "jump length".

On the other hand, the time τ is related to the periodic time τ_0 of the atomic vibrations in the lattice of the adsorbent:

$$\tau = \tau_0 e^{\frac{E}{RT}}. \tag{40}$$

From Eqns. (39) and (40) it follows that

$$D_a = D_0 e^{\frac{E}{RT}}, \tag{41}$$

where

$$D_0 = \frac{\Delta^2}{4\tau_0}.$$

TABLE 6.

Adsorbent	$\tau_0 \cdot 10^{14}$ sec
Graphite (active charcoal)	5
Al_2O_3	7.5
SiO	9.5
MgO	6.7

The values of τ_0 for various adsorbents[130] are listed in Table 6.

The activation energy is measured by observing the diffusion coefficient D_a at two neighbouring temperatures. If it is found to have the values D_1 and D_2 at temperatures T_1 and T_2, it follows from Eqn. (41) that

$$E = 4.58\,\frac{T_1T_2}{T_1-T_2}\log\frac{D_1}{D_2}. \tag{42}$$

A method[125] for determining E at two temperatures in the course of a single experiment has been described.

Dacey and Thomas investigated the rate of adsorption of a large number of substances on saran charcoal, and found that E = 1/2 to 1/3 ΔH. Hence they concluded that surface diffusion plays an essential role in the transfer of substances through charcoal. However, owing to the overlap of the adsorption fields of the opposite walls of fine micropores, molecular jumps from one wall to the other require an activation energy smaller than heat of desorption. It follows that the inequality $E < \Delta H$ may apply to matter transport through the gas phase. Measurements on other systems[44,91,131] indicate that the activation energy for the inner-diffusion process lies in the range $0.3-0.9\ \Delta H$.

Other Methods for Appraising the Role of the Migration Effect

Haul[89,90] and Timofeev and Voskresenskii[132] endeavoured to exclude volume diffusion. Haul studied the inner-diffusion rates of a number of organic vapours at low temperatures, at which the vapour pressure was low and the transport could be assumed to take place mainly in the adsorbed phase via surface migration. He determined, by means of a specially constructed balance, the centre of gravity of the adsorbate in a pellet of sorbent, and derived D_a from known equations. In his calculations Haul assumed that D_a was independent of the extent of adsorption. This, as Carman points out[133], is essentially incorrect, and casts doubts on the validity of the author's conclusions.

Timofeev and Voskresenskii[132] investigated the speed of diffusion of ethyl bromide vapour through charcoal cylinders, with and without a counter-current of a non-adsorbed gas (nitrogen). The position of the adsorption front of ethyl bromide was ascertained by X-radiography. The work was carried out at 20°, at a concentration of ethyl bromide of 20.7 to 75.9 mg litre^{-1} and under atmospheric pressure of nitrogen. Under these conditions nitrogen has practically no effect on the adsorption of ethyl bromide, and consequently the counter-current could only have affected the rate of transport of ethyl bromide in the gas phase, i.e. in pores of radius larger than the molecular mean free path. The experiments showed that the nitrogen counter-stream considerably inhibited the transport of ethyl bromide through active charcoal and thus underlined the importance of volume diffusion.

To recapitulate what has been said on the relative role of surface diffusion in transport processes at porous sorbents, it is established that this type of diffusion can contribute to the overall velocity of the process. The contribution can be a major or a minor one, according to the pore structure and the experimental conditions. With micro-porous, and fairly homogeneous sorbents, such as those described by Barrer, the flow of matter in the adsorbed phase may be comparable with that in the gas phase. With sorbents having a complex distribution of pore sizes surface diffusion may be ignored, in comparison with transport in the gas phase, when the sorption process is carried out at ordinary temperatures and, particularly, when coverage is low.

Flow of Liquid Adsorbates

Flood[93-98] considers that an increased speed of flow of adsorbed gases in porous media can result from the migration of the adsorbate in the liquid state. He bases his deduction on the following considerations.

If we assume that the thermodynamic properties of the adsorbate are the same as those which apply to the gas phase the condition for thermal equilibrium is expressed by the equation

$$v_1 dp_1 = v_2 dp_2, \tag{43}$$

where v_1 and v_2 are the volumes, and p_1 and p_2 the pressures in the gas and in the adsorbed phases respectively.

From (43) it follows that

$$p_2 = \int_0^{p_1} \frac{v_1}{v_2} dp_1 = \int_0^{p_1} \frac{\rho_2}{\rho_1} dp_1, \tag{44}$$

where ρ_1 and ρ_2 are the respective densities.

By taking the mean values of ρ_1 and ρ_2 for the pressure interval $0-p_1$, Flood obtained

$$p_2 = \left|\frac{\bar{\rho}_2}{\rho_1}\right| p_1 \quad . \tag{45}$$

Since $\rho_2/\rho_1 \gg 1$, it follows that considerable adsorbate pressures will correspond to relatively small pressure gradients in the gas phase, and give rise to a flow of adsorbate along the surface.

With the help of a number of simplifying assumptions Flood was able to derive a theoretical equation for the viscous flow in the adsorbed phase:

$$G = \frac{b}{\eta_2}\left|\frac{\bar{\rho}^2}{\rho_1}\right|\frac{\Delta p}{L}, \tag{46}$$

where η_2 is the viscosity of the liquid adsorbate, Δp the pressure drop in the gas phase, and b a constant.

Eqn. (46) leads to a more general expression for the permeability of porous media to adsorbed gases:

$$K = A\sqrt{\frac{T}{M}} + \frac{B}{\eta_1}\bar{p} + \frac{b}{\eta_2}\left|\frac{\rho_2^2}{\rho_1}\right|. \tag{47}$$

The third term on the right-hand side describes the flow of liquid adsorbate in the micropores.

The empirical equation of Flood, Tomlinson, and Leger[93] offers much better agreement with experiments results:

$$K = A\sqrt{\frac{T}{M}} + \frac{B}{\eta_1}\bar{p} + \alpha\bar{a} + \beta\frac{a_1^n - a_2^n}{\Delta p}, \tag{48}$$

where $\bar{a}$ is the mean value of the adsorption in the pressure interval Δp, a_1 and a_2 are the adsorptions corresponding to the pressures p_1 and p_2, and α, β, and n are constants.

The authors showed that Eqn. (48) applies very well to the experimental data obtained in their study of the rate of flow of the following vapours on activated charcoal: benzene, ethyl chloride, ethyl ether, and methyl alcohol.

Capillary Flow

In the region of capillary condensation capillarity forces, arising from unequal meniscus curvatures, can give rise to the transport of adsorbate[133]. To illustrate the phenomenon an idealised sorbent pore is shown in Fig.10. The vapour exerts pressures p_1 and p_2 on its ends, and an adsorbate in the state of capillary condensation fills it. The well-known Kelvin equation relates the meniscus curvature to the relative pressure:

$$\ln\frac{p_s}{p_1} = \frac{\sigma}{r_{m_1}\rho_2}\frac{M}{RT}\cos\theta_1,$$

$$\ln\frac{p_s}{p_2} = \frac{\sigma}{r_{m_2}\rho_2}\frac{M}{RT}\cos\theta_2, \tag{49}$$

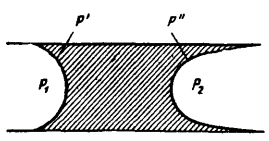


Fig.10. Liquid flow in a capillary.

where σ and ρ are the surface tension and density of the liquid adsorbate, θ the limiting contact angle, and p_s the saturated-vapour pressure. The inner pressure is related to the meniscus radius by Laplace's equation:

$$p' = \frac{\sigma \cos \theta_1}{r_{m_1}}; \quad p'' = \frac{\sigma \cos \theta_2}{r_{m_2}}. \tag{50}$$

Combining (49) and (50) we find

$$\Delta p = p'' - p' = \frac{\rho RT}{M} \ln \frac{p_1}{p_2}. \tag{51}$$

On account of this difference of pressure the adsorbate, in the state of capillary condensation, moves along the pores of the sorbent.

Special Features of the Transport of Water Vapour in Micro-Porous Adsorbents

Dacey and Thomas[124] measured the rates of adsorption of numerous substances on saran charcoal, and drew attention to the fact that water vapour adsorbs more slowly than other substances of similar molecular size. They carried out a special experiment on the rates of sorption and desorption of water vapour on three specimens of saran charcoal[134].

Up to the region of steep rise of the adsorption isotherm, water was found to behave like a gas of low molecular weight (extent of adsorption proportional to the square root of time). As the concentration and, consequently, the adsorption is increased, the effect of hydrogen bonding begins to be felt. At relatively high concentrations the rate of adsorption of water vapour becomes independent of time. The authors suggest that when the dry charcoal is exposed to a high relative pressure of water vapour the latter condenses on the outer surface and seals off the openings of the pores. As the water gradually penetrates into the very narrow pores, which can accommodate only a very few molecules, the hydrogen bonds begin to dissociate. This dissociation, according to the authors, is the rate-limiting stage of the penetration of water molecules into the depth of saran-charcoal particles. It follows that the rate of adsorption should be constant with time, as indeed is found to be the case.

CONCLUSION

A variety of methods have been applied to the study of the mechanism of transport in porous sorbents. A deeper understanding of the special features of the transport of adsorbed gases has been the result. A broad, qualitative picture of the process of transport of adsorbed gases in various regions of relative pressure, and at various coverages, can be established on the basis of existing knowledge. However, one deficiency in our understanding of the process must be pointed out. Great interest still attaches to a quantitative elucidation of the dependence of the several modes of transport on the structure of the sorbent. A few trends have been reported, but they are only the first steps in the required direction.

The structure of sorbents has received very little attention from the point of view of kinetics. Existing, quite delicate methods, e.g. those based on sorption, enable us to determine the effective dimensions of pores and their statistical distribution with sufficient precision. However, these methods are powerless to elucidate the interplay of adsorbing pores and transport pores, which is of fundamental importance to the kinetics of the process. A need exists for the development of kinetic methods of investigating the structure of porous substances. These problems are still awaiting solution.

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THE MECHANISMS OF SOME PEROXIDE REACTIONS

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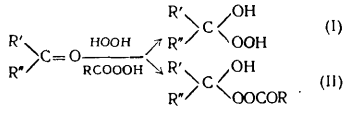
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The reactions of peroxides in organic chemistry are usually interpreted as free radical or ionic processes, but this is not always so. In addition to the large number of reactions in which free radicals are formed, there are a few in which molecules react, with the simultaneous cleavage of some bonds and formation of others; this is also true for peroxides, in which the O–O bond is known to be very reactive. Because of the low energy of the O–O bond, molecular reactions of peroxides can take place with an activation energy which is considerably less than the effective activation energy of a radical reaction. The polarity of the bonds in the peroxide group (OR, OH, and in some cases O–O) is also a factor which favours a molecular reaction. The present article is an attempt at a critical review of a large number of reactions, with the aim of finding those mechanisms which agree with the experimental facts or at least do not contradict them. In particular, we have attempted to explain the role of activated cyclic complexes in the reactions of peroxidic compounds.

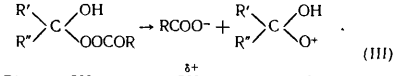
1. THE OXIDATION OF KETONES AND ALDEHYDES WITH PER-ACIDS AND HYDROGEN PEROXIDE

The oxidation of carbonyl compounds with hydrogen peroxide in the presence of acids and with mineral or organic per-acids (the Bayer–Villiger reaction[1]) is used in preparative organic chemistry to obtain acids, esters, anhydrides, and lactones[2]. The kinetics of this reaction, exemplified by the oxidation with organic per-acids of acetylcycloalkanes[3], cycloalkanones[4,5], *m*- and *p*-substituted acetophenones[6], certain other ketones[7,8], and acetaldehyde[9], shows that in almost every case the reaction obeys a kinetic equation of second order and is catalysed by acids; this agrees with a mechanism in which the first stage of the reaction is the formation of a hydroxy-peroxide of type (I) or (II) by the reaction of the carbonyl compound with hydrogen peroxide or the per-acid:

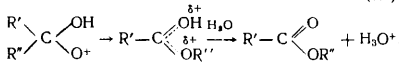


(1)

It has been suggested[10] that the second stage is the unimolecular decomposition of the hydroxy-peroxide with the formation of a stable anion and a cation with positively charged oxygen (III)*. The oxidation products of the carbonyl compound are formed as a result of the rearrangement of the cation (III):



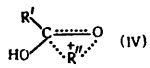
(2)



(3)

* This view point is sometimes erroneously ascribed to Criegee[11], whose views will be given when considering the rearrangement of 9-decalylaroyl peroxides.

According to another variant of this mechanism[4,12], the hydroxy-peroxide ionises to form a "non-classical" ion (IV), which rearranges to the corresponding ester with simultaneous liberation of a proton:

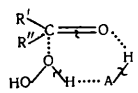

(IV)

In discussing the oxidation of ketones, it has been suggested[4,6] that stage (1) is slow and requires an acid catalyst, while the unimolecular decomposition into ions (2) and the subsequent rearrangement (3) are rapid.

The intermediate formation of compounds of types (I) and (II) in the oxidation of carbonyl compounds seems to us to be highly probable. Lyubarskii and Kagan[9] have shown experimentally that an intermediate of type (II) ($R' = R = CH_3$, $R'' = H$) is formed in the oxidation of acetaldehyde with peracetic acid; they found that there is equilibrium between the hydroxy-peroxide and the starting materials. The formation of the hydroxy-peroxide takes place in toluene with an activation energy of 7 kcal/mole and pre-exponential factor 5.2×10^5 mole^{-1} cm^3 sec^{-1}. The decomposition of the hydroxy-peroxide, which controls the reaction, requires an activation energy of about 16 kcal/mole, which is almost identical with the activation energy for the overall oxidation process found experimentally.

In a number of cases type (I) compounds have been separated as the reaction products of ketones or aldehydes with hydrogen peroxide[13]. In addition to rearranging to the corresponding esters and lactones, compounds of this type show a tendency to form cyclic and linear polymeric peroxides. Depending on the conditions of the reaction between the peroxide and the carbonyl compound, and on the relative rates of rearrangement and polymer formation of the reaction products, either compounds which do not contain active oxygen or various types of peroxidic compounds may be obtained.

The formation of hydroxy-peroxides from aldehydes is catalysed by acids and by pyridine, but is unaffected by daylight[14]. Probably this reaction, like others in which addition to carbonyl compounds takes place, passes through an activated cyclic complex of the type

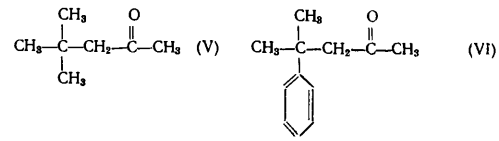


This is an example[15] of an acidic catalyst (HA = H_2O, H_3O^+, RCOOH, etc.) reacting and being regenerated in a single process.

The decomposition of the neutral hydroxy-peroxide molecule into ions [reaction (2)] requires a considerable energy uptake, even in aqueous solutions. In this respect it is extremely improbable that the activation energy of about 10–15 kcal/mole, which is normally found for the Bayer–Villiger reaction, relates to the decomposition of the hydroxy-peroxide into ions.

In chloroform, in which most kinetic studies are made, the formation of ions is energetically unfavourable, even in the case of such strong carboxylic acids as trichloracetic and trifluoracetic. When these acids react with a base such as pyridine in chloroform solution, only ion pairs of various structure are formed[16]. In the case of weaker acids such as acetic and β-chloropropionic, the reaction with pyridine leads only to the formation of complexes containing an ordinary hydrogen bond.

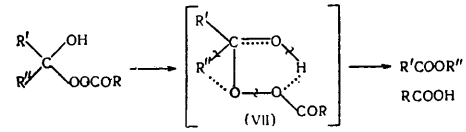
The suggestion that a cation (IV), in which the migrating group carries a partial positive charge, is formed as an intermediate, is not in accord with experimental results on the oxidation of neopentyl methyl ketone (V) and β-phenylisobutyl methyl ketone (VI) with trifluoroperacetic acid[17].


(V) (VI)

It is known that when the secondary carbon atom of the neopentyl group carries an effective positive charge (for example, in the reaction of the corresponding alkyl halide with a Friedel–Crafts catalyst), the alkyl group isomerises, with a transfer of the positive charge to the tertiary carbon atom; however, when the ketones (V) and (VI) were oxidised, only the corresponding acetates were obtained[17]. The retention of the neopentyl and β-phenylisobutyl structures during the oxidation shows that when the corresponding peroxides isomerise, the partial charge on these groups is very small or even zero.

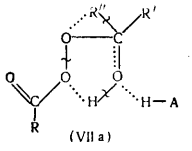
Hawthorne, Emmons, and McCallum[18] have recently shown that the ability of the alkyl groups to migrate when the phenyl alkyl ketones are oxidised with trifluoroperacetic acid changes to a considerably lesser extent than would be expected if the migrating group has carbonium-ion character. Thus, for example, the ratio of the migrating ability of the t-butyl and ethyl groups is ~ 555, while the ratio of the rates of solvolysis of the corresponding alkyl halides varies from 10^6 to 10^8. [19] This can be taken as proof that the partial positive charge on the migrating group in the oxidation of ketones is smaller than the charge on the alkyl group when the corresponding alkyl halide undergoes solvolysis. Hawthorne and coworkers consider[18] that in addition to its ability to form a carbonium ion, the volume of the migrating group has a substantial influence; with increase of the volume, the ability to migrate also increases. This is confirmed by the fact that the rate of migration of the benzyl group is commensurable with that of secondary alkyl groups, and that the neopentyl group migrates at the same rate as the ethyl group, although the carbonium ion must be more stable in the latter case. The oxidation with peracetic acid is more selective than the oxidation with trifluoroperacetic acid, which can only be explained if the migration of the alkyl group takes place simultaneously with the splitting out of the acid residue from the intermediately formed peroxide.

It seems to us more probable that the isomerisation of the hydroxy-peroxide proceeds by way of the activated six-membered cyclic complex (VII):


(4)

The existing experimental data are not sufficient for the part played by the acid in this stage of the oxidation to be definitely established. When ketones and aldehydes are oxidised with hydrogen peroxide in the absence of acids, only the corresponding ketone and aldehyde peroxides are usually formed[2,13].

The results obtained in the study of the kinetics of the oxidation of cycloalkanones, aryl alkyl ketones, and dialkyl ketones (including acetone) with trifluoroperacetic acid[20] favour the hypothesis that the decomposition of the hydroxy--peroxide is catalysed by acid and is the rate determining stage of the Bayer–Villiger reaction. It is therefore possible that the decomposition of the peroxide is more complex than Eqn. (4) would indicate. In particular, the formation of an intermediate of type (VIIa) is not excluded:



(VII a)

The acid is joined to the hydroxy group of the hydroxy--peroxide by an ordinary hydrogen bond and in some cases may transfer its proton to the peroxide molecule with the formation of an ion pair. This would facilitate the transfer of the hydrogen atom of the hydroxy group and the rearrangement as a whole.

In the transition state of the isomerisation (VII) there may be partial heterolysis of the O–O bond, but the reaction of the electron-deficient oxygen atom with the migrating alkyl group and the transfer of the hydrogen atom proceed simultaneously with the separation of charges in the O–O bond.

These views agree with the increased effectiveness of trifluoroperacetic acid as compared with perbenzoic acid. Thus, for example, methyl cyclopropyl ketone does not react with perbenzoic acid[21], but with trifluoroperacetic acid it forms cyclopropyl acetate in good yield[22].

By means of the isotope O^{18}, it has been established that in the oxidation with peracetic acid of benzophenone, 4-methoxybenzophenone[23], and fluorenone[24] in acetic acid in the presence of H_2SO_4, and in the oxidation of benzophenone with perbenzoic acid in benzene[25], the oxygen of the carbonyl group of the ketone becomes the carbonyl oxygen of the ester.

In the oxidation of optically active 3-phenylbutan-2-one with perbenzoic acid to form α-phenylethyl acetate, the configuration of the asymmetric group $C_6H_5CHCH_3$ is retained[26]. The configuration is also retained when certain ketones of the cyclohexane and cyclopentane series are oxidised[27]. All these results are in agreement with the cyclic mechanism reviewed above, and cannot be satisfactorily explained by means of processes involving the intermediate formation of kinetically free carbonium ions.

The oxidation of alkyl methyl ketones[17,22,25], acetylcycloalkanes[3], and substituted acetophenones[6] yields only the corresponding acetates. The absence of methyl esters in the reaction products of trifluoroperacetic acid with alkyl methyl ketones (alkyl = C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, iso-C_4H_9, n-C_5H_{11}, cyclo-C_3H_5) is considered[18] as confirming the mechanism according to which the migrating group is a cation stablished by hyperconjugation. However, the absence of methyl esters in the products of the oxidation, under the same conditions, of neopentyl and β-phenylisobutyl methyl ketones[22] indicates that the possible stabilisation of the hypothetical alkyl cation by hyperconjugation does not explain the ability of the alkyl group to migrate. Apparently, all other alkyl groups migrate more easily than methyl. In the oxidation of *para*-substituted benzophenones[12], the ability of the group to migrate increases with its electron-donating properties; however, cyclohexyl benzoate predominates in the oxidation products of cyclohexyl phenyl ketone[7,12]. This may probably be explained by the additional gain of energy, when the reaction goes in this direction, of the transition state (VII), because of conjugation of the phenyl ring with the system of breaking and forming bonds in the transition state. The oxidation of *ortho*--substituted benzophenones shows[28] that under otherwise equal conditions, the presence of an *ortho*-substituent may hinder the migration of the group, by preventing the conformation in which the π-electrons of the ring overlap with the partially free p-orbital of the oxygen atom to which the migrating group is joined[29].

Cyclohexyl methyl ketone reacts ten times as rapidly as acetophenone[7], probably because of the increase in the activation energy in the latter case caused by the destruction, in the transition state (IV), of the conjugation between the carbonyl and phenyl groups; this loss of conjugation is only partly compensated by the conjugation of the phenyl ring in the transition complex. In the case of the *meta*- and *para*-substituted benzophenones, the rate of reaction decreases in the series[6]:

$$p\text{-}CH_3O > p\text{-}CH_3 > m\text{-}CH_3O > H > p\text{-}Cl > p\text{-}OCOCH_3 > p\text{-}Br,$$

generally in accordance with the decrease in the electron--donor properties of the substituent groups. From the results given in Table 1 for substituted acetophenones, however, the substituent group affects the entropy of activation as well as the activation energy.

It is interesting that on passing from one group of compounds to another (Table 1), the energy, entropy, and free energy of activation change only slightly. The introduction of electron-accepting substituents (Cl, Br, $OCOCH_3$, NO_2) in the *meta*- and *para*-positions of acetophenone causes a change in the order of the reaction (first order with respect to per-acid, zero order with respect to ketone), the value of $\Delta F^{\neq}$ increasing slightly.

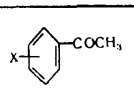
It has been suggested[6] that in the case of acetophenones containing electron-accepting substituents in the ring, the rate determining stage of the reaction is the decomposition of the per-acid into ions:

$$RCOOOH \rightarrow RCOO^- + HO^+. \qquad (5)$$

The resulting cation HO^+ is supposed to react rapidly with the ketone to form a complex, which then decomposes to the oxidation products.

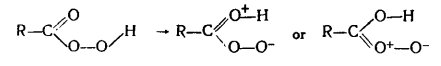
This explanation cannot be considered satisfactory. It was mentioned above that decomposition into ions, as in reaction (5), is a strongly exothermic process, and probably requires a considerably greater expenditure of energy than the observed activation energy (14–15 kcal/mole). The absence of exchange between C^{14}-benzoic acid and perbenzoic acid in chloroform at 25° [30] excludes both the possible formation of ions under these conditions and the formation of ion pairs of the type $RCOO^-HO^+$. Using C^{14} and S^{35} it has been shown[31] that there is no transfer of the hypothetical cation HO^+ even in aqueous solutions of peracetic, perbenzoic, and persulphuric acids and their anions.

Apparently, in the case of acetophenones with electron--accepting substituents, the reaction between the ketone and the per-acid is preceded by the isomerisation of the latter into some active form, as a result of which the oxidation proceeds by some mechanism other than that discussed above. To explain the considerable decrease in entropy in the transition state of the unimolecular process, it is

Ketone	$\Delta H^{\neq}$, kcal/mole	$\Delta F^{\neq}$ kcal/mole	$\Delta S^{\neq}$ e.u.	Reference
$\left[\begin{matrix}CH_3\\(CH_2)_n\end{matrix}\right]CH-CO-CH_3$				3
$n=2$	10.1	22.3	−43	
$n=3$	11.5	22.7	−40	
$n=4$	11.0	22.7	−41	
$n=5$	10.5	22.8	−43	
$(CH_2)_n\begin{matrix}CH_3\\CH_3\end{matrix}C=O$				5
$n=1$	9.1	24.0	−54	
$n=2$	15.4	22.1	−24	
$n=3$	11.6	20.7	−33	
$n=4$	13.3	24.0	−38	
$n=5$	14.7	24.3	−34	
				
$X=p$-OCH_3	11.4	23.7	−42	6
p-CH_3	11.4	24.2	−44	
m-OCH_3	14.9	24.3	−33	
p-Cl*	15.0	25.6	−37	
p-$OCOCH_3$*	14.0	25.5	−40	
m-Br*	13.9	25.6	−40	

* With these ketones the rate of reaction is independent of the ketone concentration and proportional to the per-acid concentration. In all other cases the rate of reaction is proportional both to the ketone concentration and to the per-acid concentration.

natural to suggest that the isomerisation is accompanied by a separation of charges in the per-acid molecule. A possible process is

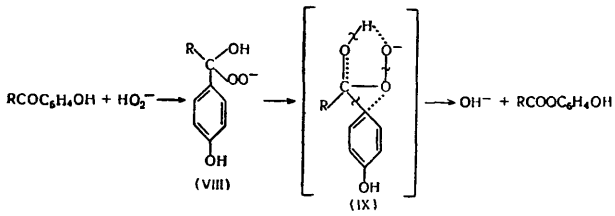


(6)

The presence of intramolecular hydrogen bonding in the ground state of the per-acid molecule facilitates the transfer of the proton.

The reason for the change in the mechanism of the oxidation of acetophenones is probably the appearance, under the influence of the electronegative substituent, of a partial positive charge on the carbon atom next to the acetyl group. In this connection it is pointed out that the oxidation of aromatic carbonyl compounds to form an ester group in alkaline medium also takes place only with compounds of a similar structure. The preparation of pyrocatechol, hydroquinone, and their derivatives by the oxidation of *o*- and *p*-hydroxybenzaldehydes and acetophenones with hydrogen peroxide in alkaline medium is known as the Dakin reaction[32].

Attempts to utilise benzoyl peroxide, lead and manganese peroxides, and silver oxide to effect reactions of this type were unsuccessful. Light, which accelerates the oxidation of benzaldehyde, does not initiate a corresponding reaction, either in the presence or in the absence of benzaldehyde. Neither sodium peroxide nor sodium perbenzoate react with *o*-hydroxybenzaldehyde in dry ether. Clearly, all these facts cannot be explained by a radical mechanism, but indicate the ionic nature of the reaction. Probably the first stage of the Dakin reaction is the addition of the ion HO_2^- to the carbonyl double bond to form the ion (VIII), which rearranges by way of the transition state (IX) to form the ester:



The dihydroxybenzene is formed on hydrolysis of the ester.

It is seen from this mechanism that an increase or decrease of the electron density at the ring atom joined to the carbonyl carbon atom will have a substantial influence on the rearrangement. An electron-donating substituent such as the hydroxy group in the *ortho*- or *para*-position will favour the reaction by increasing the electron density at the reacting atom of the aromatic nucleus; however, an electron-donating group in the position *ortho* or *para* to the carbonyl group must react with it, reducing the partial positive charge on the carbonyl carbon atom and at the same time reducing the rate of formation of the ion (VIII). Thus the factors which facilitate the second stage of the reaction inhibit the first, apparently rate-determining stage. This explains the lack of reaction in the case of certain amino and methoxy derivatives of benzaldehyde and acetophenone[32]. The introduction of the electron-accepting nitro group in position 3 of 4-hydroxybenzaldehyde causes the NO_2 and OH groups, in the *ortho*-position relative to one another, to interact so as to reduce the effect of the OH group on the carbon atom in the 1-position, so that no reaction is observed with 3-nitro-4-hydroxybenzaldehyde. For the same reason, 3-nitro-4-hydroxy-5-methoxybenzaldehyde does not react, while 2-nitro-4-hydroxybenzaldehyde and 2-nitro-3-methoxy-4-hydroxybenzaldehyde give the corresponding quinols[32]. The effects on the 1-carbon atom of the 2-nitro and 4-hydroxy groups are opposite, and it may be expected that the effect of the nitro group will prevail, reducing the electron density at the 1-carbon atom.

The decomposition of α-diketones and α-ketocarboxylic acids by hydrogen peroxide is probably analogous:

$$RCOCOR + H_2O_2 = 2RCOOH,$$

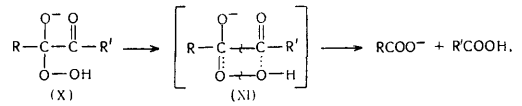
$$RCOCOOH + H_2O_2 = RCOOH + CO_2 + H_2O.$$

A study of the kinetics of this reaction[33] using diacetyl, dibenzoyl, and the sodium salts of pyruvic and benzoylformic acids has shown that the reaction is catalysed by bases. In the case of dibenzoyl and benzoylformic acid enolisation cannot take place, which shows that enolisation is not an essential step in the oxidation. The presence of acidified ferrous or ferric salts, which favours the formation of free radicals in such systems, does not cause decarboxylation of benzoylformic acid.

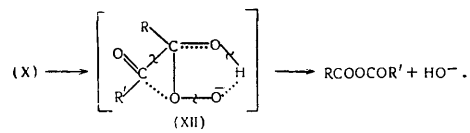
Pyruvic acid is also not decomposed in solutions containing hydrogen peroxide and ferrous sulphate, and it may even be prepared by oxidising lactic acid with Fenton's reagent[34]. These facts show that free radicals do not take part in this decomposition of ketoacids.

Bunton[33] suggests that the intermediate ion (X), formed by the reaction of the diketone (or ketoacid) with the ion

HO_2^-, decomposes by way of the four-membered activated complex (XI):

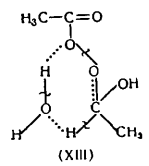


We think it probable that just as in the Dakin reaction, the ion (X) may undergo conversion by way of the six-membered transition state (XII):

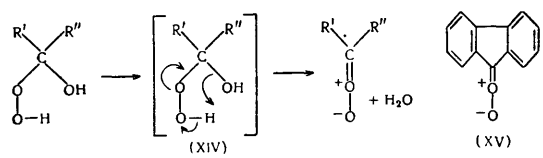


Hydrolysis of the resulting anhydride yields the acids as final reaction products.

The mechanisms reviewed above for the oxidation of carbonyl compounds are not the only possible ones. Probably, in some cases the reaction proceeds by way of an acyclic linear transition state; other types of activated cyclic complexes are also possible. Thus to explain the accelerating action of water on the decomposition of the hydroxy-peroxide formed by the peracetic-acid oxidation of acetaldehyde, Lyubarskii and Kagan[9] put forward a suggestion which is essentially that the peroxide decomposes by way of the activated cyclic complex (XIII):



Under appropriate conditions, other than those of the Bayer–Villiger reaction, ketone hydroxy-peroxides are converted to oxo-oxides, which probably play a significant part in the formation of cyclic and linear peroxides:



In the transition state (XIV), six electrons (four from the C–O and OH bonds and the unshared pair from the oxygen) move in the field of five nuclei. This is an example of a five-membered cyclic complex[35].

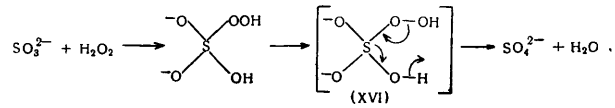
In the case of fluorenone the oxo-oxide (XV) was obtained by reacting fluorenone with hydrogen peroxide in absolute ether in the presence of dehydrating agents[36]. Fluorenone oxo-oxide is a yellow substance, m.p. 108°, soluble with difficulty in benzene and easily in methanol, while fluorenone dissolves easily in benzene and with difficulty in methanol. On cooling a solution of (XV) in acetic acid and acetic anhydride in the presence of H_2SO_4, it is partly converted to the isomeric lactone of 2-hydroxydiphenyl-2'-carboxylic acid, and partly decomposes with the evolution of oxygen and the regeneration of the starting fluorenone. The explosions which sometimes occur when attempting to prepare polymers of ketone peroxides may be due to the decomposition of the intermediate oxo-oxides of type (XV).

A general feature of the above mechanisms is the formation of intermediate products by the addition of hydrogen peroxide to the carbonyl bond. There are grounds for assuming that certain oxidation reactions of inorganic compounds also pass through the intermediate formation of corresponding addition products. It is known that the oxidation of sulphite with hydrogen peroxide in alkaline solutions follows an equation of the first order with respect to the sulphite concentration and the hydrogen peroxide concentration[37]. The activation energy at pH 10 is 15.2 kcal/mole and the pre-exponential factor 3×10^{10} litres $mole^{-1}$ sec. In addition to this reaction an acid-catalysed oxidation also takes place. It has been established by using O^{18} that in the oxidation of sulphite in acid[38] and weakly alkaline[39] solutions, oxygen is transferred to the sulphite directly from the hydrogen peroxide.

In the reduction with an aqueous sodium sulphite solution of the optically active (+)2-phenylbutane 2-hydroperoxide in the corresponding alcohol

$$ROOH + SO_3^{2-} \rightarrow ROH + SO_4^{2-},$$

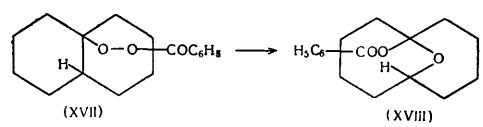
the configuration of the 1-methyl-1-phenylpropyl group is retained[40]. These facts all agree with the following mechanism for the oxidation:



In the transition state (XVI) six electrons (including two from the sulphur atom) are delocalised in the field of five nuclei.

2. THE REARRANGEMENT OF 9-DECALYL PERBENZOATE

9-Decalyl perbenzoate (XVII) is converted to the benzoic-acid ester of 1-hydroxy-1,6-epoxycyclodecane (XVIII) by heating in benzene solution[41].



The rate of reaction increases on passing from benzene solution to acetone, pyridine, chloroform, acetonitrile, and nitromethane solutions[11]. 9-Decalyl perbenzoate and peracetate react considerably more slowly than the *p*-nitroperbenzoate and trichloroperacetate. t-Butyl perbenzoate and *p*-nitroperbenzoate are more stable to rearrangement than the corresponding 9-decalyl esters.

A comparison of these data led Criegee[11] to conclude that "the cause of the rearrangement is the polarisation of the O–O bond of the per-ester, which in the (unattainable) limit would lead to the formation of the benzoate anion and a cation whose positive charge would lie on the oxygen atom".

In Criegee's opinion[11], analogous heterolysis of the O–O bond takes place in the rearrangement of the hydroxy-peroxide in the Bayer–Villiger reaction, the oxidation of

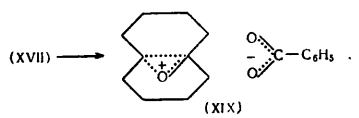
olefines and amines, the conversions of ozonides, and other reactions. In none of these cases, he considers, is there formation of free cations with positively charged oxygen.

In the rearrangement of 9-decalyl perbenzoate in methanol solutions in the presence of sodium *p*-bromobenzoate[42] and lithium *p*-nitrobenzoate[43], the resulting ester does not contain *p*-bromo or *p*-nitro-substituted aryl groups; even in the rearrangement of 9-decalyl *p*-nitroperbenzoate in the presence of lithium benzoate[43], there is no exchange of *p*-nitrobenzoyl and benzoyl groups. These results prove the intramolecular nature of the rearrangement and are in complete agreement with Criegee's views as given above.

The rate of the rearrangement in methanol solution follows an equation of the first order. The rate of reaction is increased by adding LiCl to the solution, and slightly more increased by adding HCl[42]. Even in 0.2*N* HCl the "non-catalysed" fraction of the reaction exceeds the increase in the rate caused by the presence of the HCl. The effect caused by the HCl is little different from that of the LiCl, and may be explained as a specific salt effect of the HCl. The rate of reaction increases on passing from absolute methanol to aqueous methanol[43]. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in absolute methanol are 23.1 kcal and -0.9 e.u. respectively.

Electron-withdrawing substituents in the benzene ring of the ester (XVII) (NO_2, *p*-Br) accelerate, and electron-donating substituents (*p*-CH_3, *p*-OCH_3) retard the rate of reaction[42]. The velocity constants for the substituted esters obey the Hammett equation with $\rho = 1.34$.

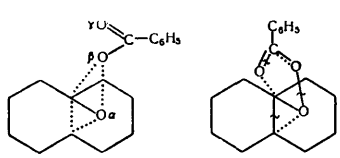
To explain the Criegee rearrangement, which has features of both an intramolecular and an "ionic" reaction[42], it has been suggested that the limiting stage is the formation of an ion pair:



(XVII) (XIX)

Denney[44,45] showed that the oxygen atoms in the COO^- group of the anion of the ion pair are not equivalent. 98% of the excess O^{18} in the carbonyl group of the original ester was found in the carbonyl group of the final rearrangement product when the reaction was carried out in methanol and in acetic acid, proving that the ion pair is not formed in this case, or that the ion pair formed during this rearrangement is unsymmetrical, one of the oxygen atoms of the anion being closer to the positively charged oxygen atom of the cation than the other.

Denney[44] suggested that the reaction passes through a transition state or intermediate compound containing a four-membered ring (XX):



(XX) (XXI)

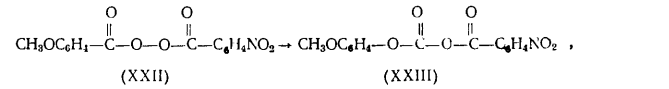
In the opinion of Denney and Denney[45], the cation in the ion pair (XIX) must be unstable, since the positive charge is on the bridgehead atom of the [4,4,1]-bicyclic system. They consider that the explanation of the reaction passing through the four-membered ring (XX) and not through the six-membered activated complex (XXI), as suggested earlier[43], is that in most of the conformations of the per-ester molecule in the normal state, the β-oxygen atom is closer to the 9-carbon atom than is the γ-atom.

Another reason why the four-membered ring is more favourable than the six-membered in the present case is the relationship between the energy of deformation of the molecule in the transition state and the change in the conjugation energy in the transition state as compared with the normal state, on the one hand, and the gain of energy because of delocalisation of the electrons of the breaking and forming bonds, on the other. In the transition state (XX) the conjugation between the carbonyl group and the phenyl ring is retained, and there is also conjugation between the carbonyl group and the transition state system. In the six-membered cyclic complex (XXI) the conjugation between the benzene ring and the carbonyl group is destroyed, but there is a gain in energy because of the formation of the benzenoid system of the transition state and its conjugation with the phenyl ring. The energy of the electrons in the ring (XXI) depends essentially on the distance between the 9-carbon atom and the oxygen of the carbonyl group, a reduction in this distance requiring energy for the deformation of the molecule. In each individual case the relationship between these factors determines which mechanism is favoured.

The recently studied[46] rearrangement of t-butyl arylpersulphonates is probably analogous to the rearrangement of 9-decalyl hydroperoxide, but with a greater separation of charges in the O–O bond.

In the rearrangement of unsymmetrically substituted aroyl peroxides, there is a competition of the mechanisms involving the four-membered and six-membered activated complexes.

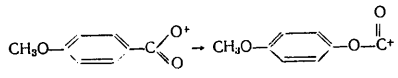
The conversion of *p*-methoxy-*p*'-nitrobenzoyl peroxide[47] (XXII) to methoxyphenyl *p*-nitrobenzoyl carbonate (XXIII) and the analogous reaction of 4-methoxy-3',5'-dinitrobenzoyl peroxide[48] (XXIV):



(XXII) (XXIII)

have features indicative of ionic reactions, among which are: (1) an increase in the rate of conversion on passing from the non-polar solvent benzene to nitrobenzene and thionyl chloride; (2) the complete absence of the ability, in the case of (XXIV), and the reduced ability, in the case of (XXII), to initiate the polymerisation of acrylonitrile and styrene under the conditions of the rearrangement; and (3) the strong catalysis by protonic acids, the action of which follows Brönsted's equation, and the catalysis by such electron acceptors as picric acid and trinitrobenzene[48]. It is interesting that in the decomposition of benzoyl peroxide, where the reaction probably takes place predominantly by way of radicals, the rate of reaction is unchanged on replacing benzene by nitrobenzene[49]. Heating (XXII) in styrene solutions causes only slight polymer formation, while with benzoyl peroxide polymerisation takes place explosively[47]. However, even in the case of benzoyl peroxide, a non-radical reaction takes place in addition to the decomposition through the intermediate formation of free radicals, as is shown by the small accelerating effect of protonic acids in acetic-acid solutions and the catalysis by acids of the $AlCl_3$ type in benzene and chloroform[50,51].

It has been suggested[47,52] that the rearrangement takes place by the heterolysis of the O–O bond with the formation of the cation (XXV) and the *p*-nitrobenzoate anion. The rearrangement of the cation XXV,

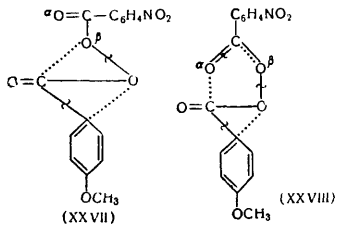


(XXV) (XXVI)

and the subsequent recombination of the cation (XXVI) with the anion would then give the reaction products.

However, experiments with *p*-methoxy-*p'*-nitrobenzoyl peroxide labelled with O^{18} in the anisoyl carbonyl group[53] have shown that the *p*-methoxyphenol formed by the hydrolysis of the rearrangement product does not contain the excess O^{18}. Thus in this case also there is no formation of a cation with a positively charged monovalent oxygen atom. Since such a cation is not formed even with such favourable structural factors, and in a solvent such as thionyl chloride, it is doubtful whether hypothetical ions of this type take part in other reactions and with other less favourable conditions.

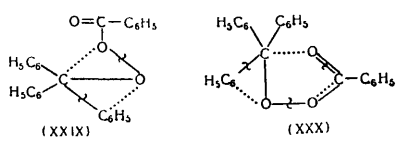
The above experimental results can be satisfactorily explained if the reaction is considered to pass through an activated four-membered (XXVII) or six-membered (XXVIII) complex:



(XXVII) (XXVIII)

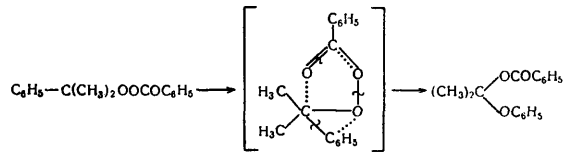
Analysis of the rearrangement products of *p*-methoxy-*p'*-nitrobenzoyl peroxide labelled with O^{18} in the *p*-nitrobenzoyl carbonyl group[45] has shown that only 66% of the carbonyl oxygen is retained during the rearrangement. Clearly in this case the reaction does not pass solely through the four-membered transition state (XXVII), in which the carbonyl oxygen remains in the carbonyl group of the rearrangement product, but also passes through the six-membered complex (XXVIII).

Denney and Denney[45] have noted that in the case of *p*-methoxy-*p'*-nitrobenzoyl peroxide, steric effects are less apparent than for *trans*-9-decalyl perbenzoate, but here also, in the majority of conformations, the β-oxygen atom is nearer the anisoyl carbonyl carbon atom than is the α-oxygen. When the distortion of the valency angles requires less energy, the six-membered cyclic complexes may apparently be expected to play a greater part in the reaction. In this connection, the conversion of triphenylmethyl perbenzoate to phenoxydiphenylmethyl benzoate is of interest, since a four-membered (XXIX) and a six-membered (XXX) activated complex are both theoretically possible.

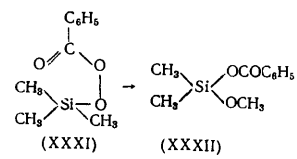


(XXIX) (XXX)

For both mechanisms there is a substantial conjugation between the cyclic transition-state system and the neighbouring groups. Thus, for example, the rearrangement of triphenylmethyl perbenzoate is so rapid, that on causing benzoyl chloride to react with triphenylmethyl hydroperoxide, only its rearrangement product, phenoxydiphenylmethyl benzoate, is obtained[54]. On the other hand, dimethylphenylmethyl perbenzoate[55] is relatively stable, melting at 45°, and slowly decomposing on keeping according to the reaction



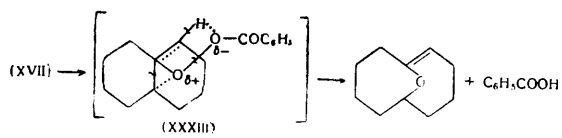
The rearrangement of trimethylsilyl perbenzoate (XXXI) to dimethylmethoxysilyl benzoate[56] (XXXII) probably belongs to this type of reaction:



(XXXI) (XXXII)

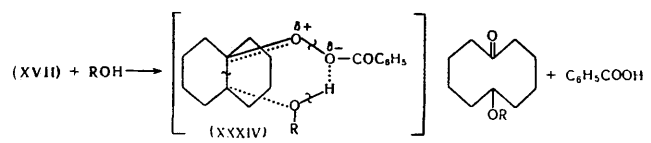
It is interesting that in the rearrangement of silyl per-esters, as with alkyl per-esters, the phenyl group migrates more easily than the methyl group.

The elimination of benzoic acid (7) which accompanies the rearrangement of *trans*-9-decalyl perbenzoate[42] probably takes place by way of the activated six-membered cyclic complex (XXXIII), the formation of which does not meet with the steric hindrance mentioned above:



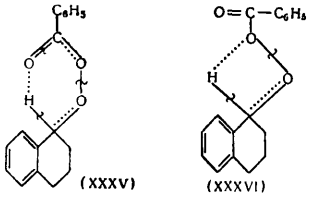
(7)

Goering and Olson[43] have obtained evidence that in the solvolysis of the per-ester (XVII), which takes place in addition to the rearrangement in aqueous methanol, the per-ester molecule undergoes the same changes as in the rearrangement. It is possible that in this case the separation of charges in the O–O bond is accompanied by the close approach of a solvent molecule to the per-ester molecule, so that the reaction passes through the activated six-membered cyclic complex (XXXIV):



The decomposition of 1-tetralyl perbenzoate to benzoic acid and α-tetralone is another example of the rearrangement of a hydroperoxide ester in which polarisation of the O–O bond plays a substantial part. In this case also, the

reaction can pass through the activated cyclic complexes (XXXV) and (XXXVI):



(XXXV) (XXXVI)

The decomposition of the terephthalic esters of isopropyl and n-propyl hydroperoxides with the formation of acetone and propionaldehyde respectively[57] belongs to this type of reaction. The formation of alcohols and carbonyl compounds by the decomposition of secondary and tertiary hydroperoxides is catalysed by acids[58-63]. The decomposition of cumene hydroperoxide, which is the basis of the industrial production of phenol and acetone[59,64,65], has been studied in greatest detail.

Isopropylbenzene hydroperoxide remains unchanged over a prolonged period of time in glacial acetic acid at room temperature. In the presence of strong acids ($HClO_4$, etc.), it decomposes quantitatively into phenol and acetone[60]. The reaction takes place at an observable rate even at -80°. Under these conditions, hydrogen chloride is a less effective catalyst, although even traces of HCl in pure cumene hydroperoxide cause explosive decomposition, probably because the process is strongly exothermic[66]. In alcoholic solution ferric chloride does not catalyst the reaction, but in benzene $FeCl_3$ is a strong Lewis acid and accelerates the decomposition of cumene hydroperoxide into phenol and acetone. Boron trifluoride, aluminium chloride, and sulphuric acid in benzene and dioxane, act analogously[60].

The rate of the reaction is proportional to the hydroperoxide concentration[67-70]. In 50% acetic acid in the presence of small amounts (up to 0.2 M) of *p*-toluenesulphonic acid and with the ionic strength of the solution maintained constant with lithium chloride, the rate of reaction is proportional to the acid concentration[67]. The reaction is not catalysed by molecular acetic acid. In 50% aqueous alcoholic solutions containing HCl, $HClO_4$, or $CH_3C_6H_4SO_3H$, the rate of reaction increases on adding the corresponding lithium salts in proportion to the increase in acidity of the solutions[70]. The acid concentration in these experiments did not exceed 0.5 M, and the total electrolyte concentration was not more than 2.5 M. In the equation relating the velocity constant to the acidity function of the solution,

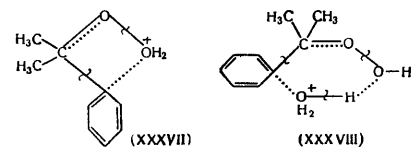
$$\log k = a - \rho H_0,$$

the values of the coefficient ρ for the various solutions were: $HClO_4 - LiClO_4$ 1.45; HCl – LiCl 1.01; and $CH_3C_6H_4SO_3H - CH_3C_6H_4SO_3Li$ 0.76.

The occurrence of a linear relationship between the logarithm of the observed velocity constant and the acidity function is usually considered an indication that the mechanism is one in which the rate determining stage is the unimolecular decomposition of a protonated substrate molecule[71,72]. Without entering the discussion[73,74] as to the validity of this criterion, we note that the existing experimental data are insufficient for selecting any one particular detailed mechanism for the decomposition of the hydroperoxide. If the hydroperoxide is protonated in these solutions, the activation energy for the reaction, 21 kcal/mole, includes the energy required for the protonation of the hydroperoxide (8–9 kcal/mole[75,76]) and the activation energy for the rate-determining step.

Apparently the existence of cations with positively charged oxygen[60,62] or carbon[67] atoms in weakly acid solutions is as improbable as in the other rearrangements of peroxides and oxidation reactions whose mechanisms were discussed above. The absence of the formation of a stable cation with positively charged oxygen in the decomposition of 1-phenylethyl hydroperoxide in acid solution is proved[77] by the absence of exchange between the unreacted hydroperoxide and H_2O^{18}.

The conversion of cumene hydroperoxide probably takes place through the activated cyclic complexes (XXXVII) or (XXXVIII):



(XXXVII) (XXXVIII)

It is possible that in non-aqueous solutions in the presence of Lewis acids the reaction passes through a transition state of structure analogous to (XXXVII).

The activation energy for the decomposition of *p*-nitrocumene hydroperoxide is 6.6 kcal greater than for cumene hydroperoxide; this agrees with the structures (XXXVII) and (XXXVIII), since for *p*-nitrocumene hydroperoxide the formation of the transition state will require additional energy to decrease the positive charge in the position *para* to the nitro group. The energy of conjugation of the nitro group with the phenyl ring in nitrobenzene is probably[78] not more than the above difference in the activation energies for cumene hydroperoxide and its *p*-nitro derivative.

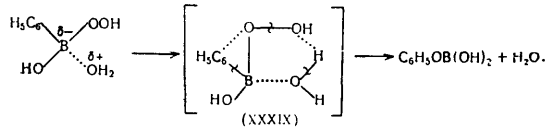
Activated cyclic complexes probably also take part in the oxidation of phenylboric acid by hydrogen peroxide and peroxidic compounds:

$$C_6H_5-B(OH)_2 + H_2O_2 = C_6H_5OH + B(OH)_3.$$

When phenylboric acid labelled with O^{18} is oxidised in water enriched in H_2O^{18} with ordinary hydrogen peroxide, the phenol formed has the normal content of oxygen isotopes[79]. A similar result was obtained in the oxidation of [O^{18}]phenylboric acid with 1,2,3,4-tetralyl hydroperoxide in O^{18}-aqueous dioxane. When phenylboric acid is oxidised with optically active 1-phenylethyl hydroperoxide, the configuration of the 1-phenylethyl radical is retained[79]. The rate of the reaction is first order with respect to the hydrogen peroxide concentration. At pH values of 2–6, in addition to a first-order reaction with respect to phenylboric acid, another reaction occurs, the rate of which is proportional to the square of the acid concentration. At pH 1.5–3 the rate of reaction is independent of pH. On increasing the hydrogen-ion concentration, an acid-catalysed reaction appears, whose rate is determined by the acidity function of the solution[81]. The reaction presumably passes through the intermediate formation of phenylboric acid hydroperoxide, $C_6H_5B(OH)OOH$, which rearranges to give the oxidation products[80,81]. The conversion of this hydroperoxide probably takes place, as in the case of tertiary alkyl hydroperoxides, by way of transition states of type (XXIX) to the easily hydrolysed phenylborate $C_6H_5OB(OH)_2$, or by way of an activated cyclic complex, similar to (XXXVII), to phenol and metaboric acid, which is then hydrated.

However, it may also be considered that in aqueous solutions the phenylboric acid reacts in the hydrated form, because of the vacant atomic orbital of the boron. The above experimental data agree with the mechanism by which the

reaction passes through the activated cyclic six-membered complex (XXXIX):

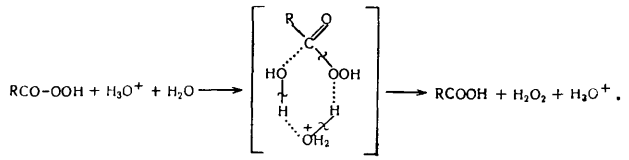


(XXXIX)

The reaction of the boron atom with the water molecule, because of its vacant orbital, increases its acidic properties, and facilitates the transfer of the hydrogen atom in the active cyclic complex (XXXIX). In solutions of acids the complex of the phenylboric acid hydroperoxide with water becomes protonated and the protonated complex reacts. The increase in the rate of reaction is proportional to the pH in the pH range 3–6, probably because of the splitting out of a hydrogen ion from the peroxide group.

3. THE HYDROLYSIS OF PER-ACIDS AND THE REACTION OF HYDROGEN PEROXIDE WITH ALCOHOLS

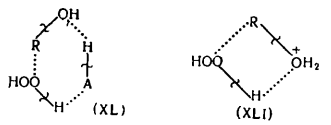
The hydrolysis of per-acids yields the corresponding acid and hydrogen peroxide. Using O^{18} and organic per-acids, it has been established[24] that the reaction proceeds with cleavage of the acyl–oxygen bond. Kinetic measurements in solutions of perchloric acid, which accelerates the reaction, have shown that the rate of reaction is proportional to the hydrogen-ion concentration and not the acidity of the solution. The absence of a salt effect, which is specific for reactions whose rate is proportional to the acidity of the solution[70,82], makes it unnecessary to consider a mechanism involving protonation of the per-acid molecule and unimolecular decomposition of the protonated molecule. The experimental facts can be satisfactorily explained on the basis of the mechanism which has already been put forward for certain hydrolysis reactions of organic esters[83]:



The reaction of tertiary and certain secondary alcohols with 30% hydrogen peroxide in excess 70% sulphuric acid[84-87] or their reaction with concentrated (85–90%) hydrogen peroxide in the presence of small quantities of concentrated mineral acids[88-92] leads to the formation of the corresponding hydroperoxides. Using alcohols containing O^{18} in the hydroxyl group, it has been established that the reaction proceeds with cleavage of the alkyl–oxygen bond[77]. Analysis of the experimental data[89,90] shows that the polarity of this bond has a substantial influence on the reaction.

When optically active 1,2,3,4-tetrahydronaphthol is reacted with 85–90% H_2O_2 in the presence of H_2SO_4, the inactive hydroperoxide is formed[89]; this can be considered proof that in this case there is intermediate formation of carbonium ions.

The formation of carbonium ions is the limiting stage in the heterolysis of the C–O bond, and is apparently by no means always realised; thus, for example, the reaction of *trans*-decalol with concentrated H_2O_2 in the presence of H_2SO_4 yields the *trans*-hydroperoxide[89]; optically active 2-phenylbutan-2-ol and its acid phthalate give 1-methyl-1-phenylpropyl hydroperoxide in which the configuration of the carbon skeleton is to a large part retained, both in acid and neutral conditions[41]. An analogous result was obtained in the reaction of 1-phenylbutanol and 2'-(1-naphthyl)ethanol with H_2O_2 in the presence of H_2SO_4.[91] Apparently, the hydrogen peroxide molecule acts as an acid in the neutral conditions. This reaction, like certain esterification reactions of alcohols in which the alkyl–oxygen bond is broken, probably passes through activated cyclic complexes[83] of type (XL) and (XLI):

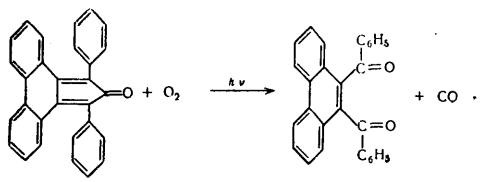


(XL) (XLI)

The reactions in which inversion of the configuration predominates, as is observed in the case of 1-phenylethanol[92], or 1-phenylpropanol and 1-phenylethyl ether[91], probably combine the cyclic mechanisms with mechanisms in which carbonium ions are formed as part of ion pairs.

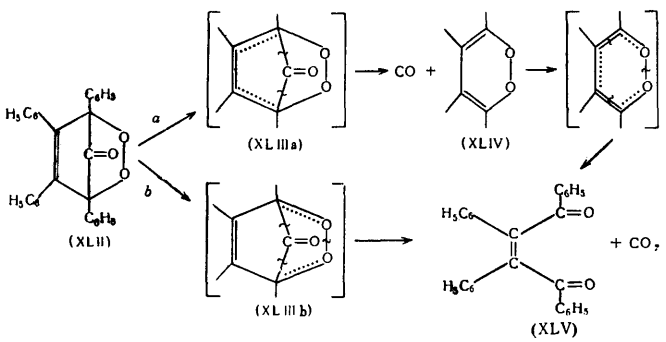
4. THE THERMAL DECOMPOSITION OF PEROXIDES

In the photochemical oxidation of arylcyclopentadienes, carbon monoxide is split off, and there is no formation of transannular peroxides as in the case of other dienoid hydrocarbons[93]; thus, for example, phencyclone, on standing in toluene solutions in the light, is oxidised by the oxygen of the air to form dibenzoylphenanthrene[94]:



Under analogous conditions acecyclone is converted to dibenzoylacenaphthylene.

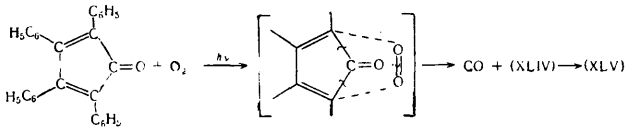
The sensitised photo-oxidation of tetraphenylcyclopentadienone proceeds very smoothly, with splitting out of CO and formation of *cis*-dibenzoylstilbene[95]. It can be assumed that the transannular peroxide (XLII) is first formed,



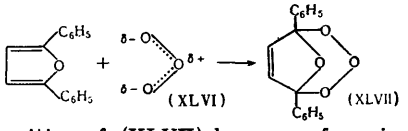
(XLII) (XLIIIa) (XLIV) (XLIIIb) (XLV)

and then decomposes with a transition state (XLIIIb) to the final reaction product (XLV), or gives the intermediate peroxide (XLIV) which then isomerises to (XLV). We have already suggested an analogous mechanism for the splitting

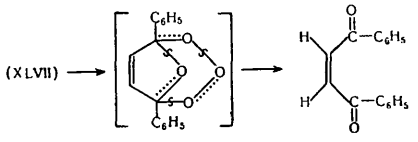
out of CO from the adducts of cyclopentadienones with dienophilic reagents[96]. As in this case, the reaction passes through a transition state (XLIIIa) or (XLIIIb), in which six electrons move in the field of five nuclei. This is an example of a five-membered cyclic complex. In addition to the conjugation between the phenyl rings and the "aromatic" system of the transition state, the fact that two electrons of the transition complex are transferred to the bonding orbital of the CO molecule also plays a substantial part in the reaction. The question of which of the two routes (*a* or *b*) is taken by the reaction has not been satisfactorily settled. This depends not only on the energy of the breaking bonds, but also on the energy of conjugation in the active complex. A third route is also theoretically possible, in which the cyclopentadienone reacts with the oxygen molecule to split out CO and form the peroxide (XLIV), which rapidly isomerises to *cis*-dibenzoylstilbene:



It is probable that in certain ozonolysis reactions the decomposition of the peroxides passes through activated cyclic complexes. For example, in the ozonation of 2,5-diphenylfuran (XLVI) in acetone or methanol at -40°, after the absorption of one mole of ozone per mole of (XLVI), *cis*-1,2-dibenzoylethylene can be separated, instead of the expected product in which the double bonds of the original furan have been split[97]. The first stage of the reaction may be the addition of the ozone molecule to the 1,4-position of the diene system of the 2,5-diphenylfuran to form the peroxide (XLVII):



The decomposition of (XLVII) by way of a six-membered cyclic complex yields the *cis*-1,2-dibenzoylethylene:



The *cis*-configuration of the benzoyl groups is in agreement with the suggested opening of the furan ring after the formation of a double bond between these atoms.

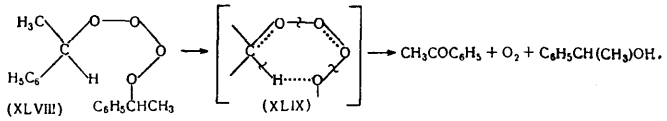
The idea of an activated cyclic complex was recently put forward in discussing the mechanism of the oxidation of alkylbenzenes with oxygen[98]. The rate of oxidation of cumene, ethylbenzene, and some of their deuterated derivatives in the presence of azodiisobutyronitrile is independent of the oxygen pressure in the range 200–760 mm Hg. This is considered proof that only peroxide radicals take part in the breaking of the chain reaction. In the oxidation of cumene and α-*D*-cumene the yield of hydroperoxide is 96–98% and is independent of the chain length (the ratio of the number of oxidised molecules to the number of initiating particles). This confirms the suggestion[99] that the peroxide radicals react as follows:

$$2C_6H_5C(CH_3)_2OO\cdot \rightarrow C_6H_5C(CH_3)_2OOH + C_6H_5CCH_3{=}CH_2 + O_2.$$

In the case of ethylbenzene the yield of hydroperoxide varies from 64 to 85% and increases with increase of the chain length, indicating the formation in the chain-breaking reaction of oxygen-containing compounds which are not peroxides. The amount of acetophenone formed in this reaction agrees with the suggested chain-breaking step:

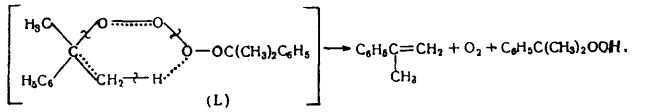
$$2C_6H_5CHCH_3OO\cdot \rightarrow C_6H_5COCH_3 + C_6H_5CHOHCH_3 + O_2.$$

The presence of an isotope effect in the chain-breaking reaction ($k_H/k_D = 1.9$) shows that the C–H bond is broken in the rate-determining stage of this reaction. It is supposed that in the case of ethylbenzene the peroxide radicals recombine to form the peroxide (XLVIII):



The peroxide (XLVIII), which is in equilibrium with the original peroxide radicals, decomposes by way of the six-membered activated complex (XLIX) to form acetophenone, oxygen, and α-phenetole.

It may be supposed that in the case of cumene an analogous dimeric peroxide is formed, decomposing through the transition state (L):

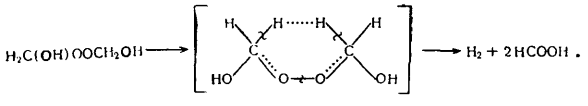


The cleavage in (L) of a C–H bond more stable than in (XLIX) and the cleavage of an O–O bond in (XLIX) instead of a C–O bond in (L) explain, in our view, the longer chain length in the oxidation of cumene as compared with the oxidation of ethylbenzene (10–25 as against 2–4). Russel[98] suggests that an analogous chain-breaking mechanism takes place in the photosensitised oxidation of ethanol[100].

The reaction of hydrogen peroxide with formaldehyde in alkaline solutions[101] (used for the quantitative determination of formaldehyde) takes place according to the equation

$$2CH_2O + H_2O_2 + 2NaOH \rightarrow H_2 + NaOOCH + 2H_2O.$$

Wieland and Wingler[102] studied this reaction and concluded that the hydrogen is evolved in the molecular and not the atomic form, since under the reaction conditions methylene blue is not decolourised. This is confirmed by the absence of HD or D_2 when the reaction is carried out in D_2O solution[103]. Wieland and Wingler considered that the reaction proceeds through the intermediate formation of di(hydroxymethyl) peroxide, which decomposes as follows:



The decomposition of primary hydroperoxides to form hydrogen and the corresponding acid[104–106] apparently also takes place through the intermediate formation of alkyl hydroxyalkyl peroxides. The thermal decomposition of n-butyl hydroperoxide has been studied in detail[106–108]. At 80°–100° the main reaction products are hydrogen and butyric acid in equimolecular quantities[107], others being propane, carbon monoxide, carbon dioxide, water, butyl butyrate, butyraldehyde, butanol, butyl formate, and propionic acid. The amount of gas given off in the decomposition of n-butyl hydroperoxide in a quartz flask in ultra-violet light at 25° is not more than a third of the amount

obtained by thermal decomposition at 86°, the yield of hydrogen, acid, and butyl butyrate being less and the yield of methane, propane, butanol, and butyl formate being more, which indicates that the latter are formed by free-radical reactions, while the former are products of non-radical reactions.

The hydrogen given off in the decomposition of n-butyl deuteroperoxide does not contain D_2 or HD:[107]

$$C_3H_7CH_2OOD \rightarrow C_3H_7C(=O)-OD + H_2.$$

Experiments in which the hydroperoxide was decomposed in the presence of D_2 showed that the hydrogen formed does not exchange with deuterium, no HD being formed. Under the same conditions, the decomposition of t-butyl hydroperoxide and the reaction of cobaltous cyanide with water[108] are accompanied by exchange. These experiments, like those with methylene blue[108], show that when n-butyl hydroperoxide decomposes, hydrogen is given off in the molecular and not in the atomic form.

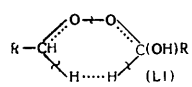
In the absence of aldehydes there is an induction period; in the presence of a small quantity of butyraldehyde there is no induction period and decomposition takes place more rapidly. This confirms the suggestion[108] that the hydrogen is split off from the aldehyde-peroxide compound, and not from the peroxide itself. The induction period is therefore that time in which the aldehyde concentration, and so the intermediate aldehyde-peroxide compound concentration, becomes sufficiently great for the reaction to be observable. The aldehyde is probably formed in accordance with the equation

$$RCH_2OOH \rightarrow RCHO + H_2O.$$

At room temperature, n-butyl 1-hydroxyalkyl peroxides, the suggested intermediates in this reaction, are formed rapidly.

Experiments on the decomposition of n-butyl 1-hydroxyalkyl peroxides, where alkyl = methyl, ethyl, and butyl, have shown that the main products, as in the case of n-butyl hydroperoxide, are hydrogen, the corresponding acid, and butyraldehyde. When n-butyl hydroperoxide is decomposed, hydrogen, butyric acid, and butyraldehyde are formed in equimolecular amounts. When n-butyl 1-hydroxybutyl peroxide decomposes in the presence of toluenesulphonic acid, the amount of hydrogen given off is only one-fifth of the amount obtained in the thermal decomposition. In the presence of alkali, n-butyl 1-hydroxyethyl and n-butyl 1-hydroxybutyl peroxides decompose rapidly, but unlike the decomposition of n-butyl 1-hydroxymethyl peroxide, no hydrogen is formed. Thus the thermal decomposition of these compounds is not catalysed by acids or bases.

From a comparison of the results obtained in this study, the authors concluded that during the reaction there is reversible formation of the butyl 1-hydroxyalkyl peroxides, which decompose with loss of hydrogen by way of the transition state (LI):



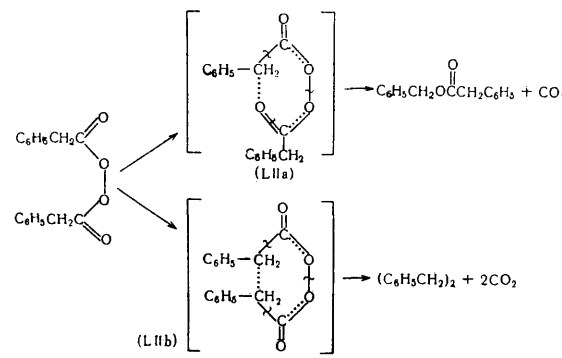
(LI)

The decomposition of per-acids, per-esters, and acyl peroxides with the evolution of CO_2 sometimes takes place completely or partially by a molecular mechanism without the participation of free radicals. It must be said here that in many cases it is difficult or even impossible to distinguish a molecular reaction from a radical reaction in a "cage" of solvent[109] (the "cage" effect). The cage effect is considered below.

Phenylacetyl peroxide[110] decomposes at 0° somewhat more rapidly than does benzoyl peroxide at 70°. When the reaction is carried out in *o*-chlorotoluene, no chlorine-containing products are obtained; however, in addition to the molecular reaction, a radical mechanism is operative to a certain extent, because when the reaction is carried out in the presence of oxygen or iodine, some benzaldehyde or benzyl iodide is formed, and because the velocity constant of the reaction depends on the initial peroxide concentration. The reaction is strongly catalysed by acids, the velocity constant increasing with the dissociation constant of the acid in water in accordance with Brönsted's equation. These authors consider that the results cannot be completely explained by an ionic or radical mechanism, which affect only the O–O bond, and in addition to mechanisms of the type

$$\begin{array}{l} C_6H_5CH_2-CO \\ \quad\quad | \\ C_6H_5CH_2-CO \\ \quad\quad \| \\ \quad\quad O \end{array} \rightarrow \begin{array}{l} C_6H_5CH_2^{\cdot} + CO_2 + C_6H_5CH_2-COO^{\cdot} \\ C_6H_5CH_2^{+} + CO_2 + C_6H_5CH_2-COO^{-}, \end{array}$$

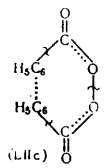
they consider it necessary to introduce mechanisms involving cyclic complexes of the type (LIIa) or (LIIb) to explain the increased rate:



Because there is no conjugation between the phenyl ring and the carbonyl group, in phenylacetyl peroxide the cleavage of the O–O bond to form free carboxyl radicals is less probable than in the case of benzoyl peroxide, and decomposition by way of the cyclic active complexes of type (LIIa) and (LIIb) becomes more probable, since the conjugation between the phenyl rings and the activated-cyclic-complex system is a source of further reduction in the activation energy. These are apparently the two basic reasons why phenylacetyl peroxide, as opposed to benzoyl peroxide, decomposes by a non-radical route. The same arguments against the presence of ions in such media as toluene and carbon tetrachloride may be adduced as in the discussion of the mechanism of the oxidation of ketones by per-acids and the rearrangements of aroyl peroxides.

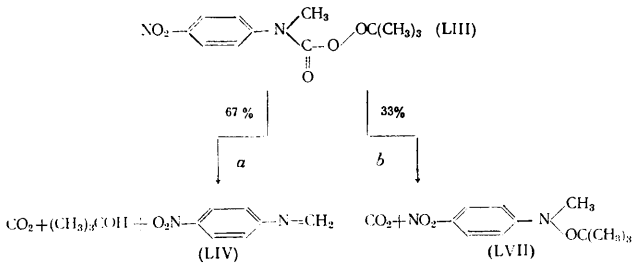
Razuvaev[111] recently showed that the diphenyl formed in the photochemical decomposition of benzoyl peroxide in [C^{14}]benzene does not contain labelled phenyl groups, in agreement with the mechanism in which the photo-activated benzoyl peroxide molecule decomposes by way of a cyclic

transition state of type (LIIc):



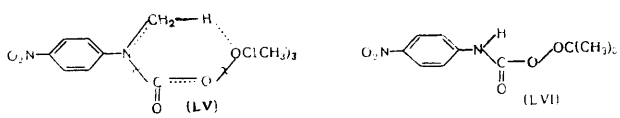
(LIIc)

Pedersen[112] has recently studied an interesting case of photochemical decomposition in a crystal. He found that t-butyl *N*-methyl-*N*-(*p*-nitrophenyl)percarbamate (LIII) decomposes at 30° with a half-decomposition period of 2 days by two routes:



(LIV) (LVII)

In the presence of moisture *N*-methylene-*p*-nitraniline [(LIV), identified by its infra-red spectrum] is rapidly hydrolysed to form formaldehyde and *N*,*N*'-methylene-bis-*p*-nitraniline; in the absence of moisture no formaldehyde is formed. In Pedersen's opinion, the decomposition of (LIII) to form (LIV) is an intramolecular reaction passing through the cyclic transition state (LV):

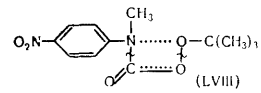


(LV) (LVI)

As proof of this, he showed that t-butyl *N*-(*p*-nitrophenyl)-percarbamate (LVI), for which a similar mechanism is impossible, is much more stable than (LIII), the half-decomposition period being 600 days at room temperature. Similarly liquid $(CH_3)_2NCOOOC(CH_3)_3$ decomposes more rapidly (half-period 65 days) than crystalline $C_2H_5NHCOOOC(CH_3)_3$ (half-period 800 days).

Pedersen considers that the increased rate of decomposition of (LIII) as compared with (LVI) is due to the possibility of the reaction passing through the six-membered cyclic complex, whose formation is facilitated by the ready decomposition of the molecule in the crystal. In cumene solution at 50°–80°, (LIII) and (LVI) decompose into free radicals (the polymerisation of styrene is initiated) with subsequent formation of CO_2 and *N*-methyl-*p*-nitraniline and *p*-nitraniline respectively.

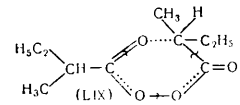
The decomposition of (LIII) to (LIV) is strongly exothermic. According to Pedersen[112], the energy of this process enables neighbouring molecules of (LIII) to decompose with the liberation of CO_2 and the formation of free radicals, which then recombine to give (LVII). The absence of acetone among the reaction products is explained by the cage effect, which favours the recombination of the free radicals, and by the low energy of the radicals formed. However, it cannot be said that the formation of (LVII) (reaction *b*) does not take place by an intramolecular reaction passing through the four-membered ring (LVIII) and so requiring a higher activation energy than reaction *a*:



(LVIII)

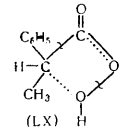
Another possible intramolecular mechanism involves the conversion of the peroxide to a carbonate as an intermediate stage[112].

Certain results obtained with the peroxides of optically active acyl groups indicate the existence of molecular as well as radical processes in the decomposition of acyl peroxides. In the decomposition of (+)α-methylbutyryl peroxide in α-trichlorotoluene[113], s-butyl α-methylbutyrate is formed in 30–40% yield, and on hydrolysis gives optically active s-butanol of the same configuration with respect to the asymmetric carbon atom as the original peroxide. The optically active ester may be formed by way of the cyclic activated complex (LIX):



(LIX)

In the reaction of sodium peroxide with α-phenylpropionyl chloride[114] in a mixture of ether with a little water or in aqueous solution at -15°, instead of the corresponding per-acid or peroxide, α-phenylethyl α-phenylpropionate, 2,3-diphenylbutane, α-phenylethanol, acetophenone, and styrene are obtained. The alcoholic portion of the α-phenethyl α-phenylpropionate and the α-phenylethanol are optically active and retain the configuration of the original α-phenylethyl group, but with 25–50% racemisation. It may be considered that in this case the ester is formed by a combination of a radical and an intramolecular reaction. Control experiments have shown that α-phenylethanol is not a hydrolysis product of the ester under the reaction conditions and is not formed by other reactions during its separation from the reaction mixture. Greene[114] considers that the formation of the alcohol retaining the configuration of the α-phenylethyl group is the result of the decomposition of the per-acid formed, by way of the cyclic four-membered activated complex (LX):

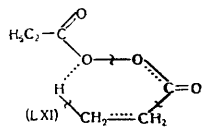


(LX)

In the decomposition of optically active β-phenylisobutyryl peroxide, the alcoholic portion of the ester formed retains the configuration of the original 1-phenyl-2-propyl group to the extent of 90%,[115] which may be considered to be in agreement with the hypothesis that the peroxide decomposes by way of a cyclic activated complex of type (LIX). De Tar and Weiss[115] have remarked that since there is no reason for thinking that more than one intramolecular mechanism for the rearrangement exists, to explain the partial racemisation it is necessary to assume that some of the ester is formed in a free-radical reaction. The varying amounts of racemic ester formed in each individual decomposition of a peroxide are caused not only by the differences in the activation energy for the inversion of the free alkyl radical, but also by the varying parts played by free-radical reactions in each individual case.

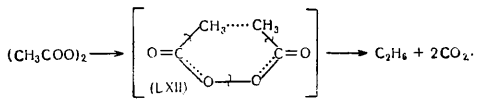
In other cases of the decomposition of acyl peroxides, the results enable ideas on the competition of radical and intramolecular processes to be more soundly based.

In the decomposition of propionyl peroxide[116] in solution in isooctane at 65° in the presence of inhibitors (*p*-benzoquinone, iodine), a certain quantity of the ethylene and ethane formed is independent of the concentration and nature of the inhibitor and remains constant when they are changed; this may be explained either by assuming that the decomposition takes place by way of a cyclic activated complex, or by assuming that the ethyl radicals formed by the decomposition of $C_2H_5COO\cdot$ disproportionate in a "cage" of solvent. In the latter case, the ratio $C_2H_6 : C_2H_4$ should be one, but it has been established mass-spectrometrically and by hydrogenation that this ratio is close to 0.35; the quantity of ethylene formed is therefore almost three times the quantity expected if it is formed only by disproportionation of ethyl radicals. The authors therefore conclude that in addition to the disproportionation of radicals in the solvent cage, in the present case an intramolecular reaction also takes place, probably by way of the cyclic active complex (LXI):



(LXI)

The decomposition products of acetyl peroxide in dilute solutions of isooctane are methane, ethane, carbon dioxide, and the disproportionation products of isooctyl radicals[117]. The yield of ethane is decreased as the temperature increases; this disproves the suggestion that the source of the ethane is the bimolecular recombination of free methyl or acetate radicals, since the concentration of these radicals increases with temperature. If the reaction is carried out in the presence of iodine at 85°, the rate of reaction is unchanged, the yield of methane is greatly reduced, and the yield of ethane remains unchanged. These results can be explained either by the assumption that the ethane is formed as a result of the recombination of radicals in a solvent "cage", or by the hypothesis that the source of the ethane is an intramolecular reaction passing through the cyclic activated complex (LXII):



(LXII)

This reaction should apparently proceed at the same rate in the liquid and gaseous phases. Indeed, ethane is the main product in the decomposition of acetyl peroxide vapour[118]. However, when the reaction is carried out in the gaseous phase (initial partial pressure of acetyl peroxide 0.1 mm and of toluene 15 mm Hg) at 188° in the presence of iodine[119] the yield of ethane falls almost to zero, even with an iodine vapour pressure of only 0.23 mm Hg. The rate of reaction is independent of the iodine concentration, showing that the peroxide does not react with the iodine. On the basis of these results, it was concluded[118] that ethane appears in the reaction products exclusively as a result of the recombination of methyl radicals. Apparently, the first stage of the reaction is the decomposition of the molecule into acyloxy radicals, as was found in the case of the thermal uninitiated decomposition of benzoyl peroxide[49,120-122]. The methyl radicals are formed, according to this mechanism, as the result of decarboxylation of the acyloxy radicals*. The recombination of radicals immediately after their formation has been called "primary recombination"[109].

5. THE CAGE EFFECT

Let us suppose that in a gas two radicals are formed at a certain moment of time as a result of a reaction; they fly apart in opposite directions and each particle before its next collision traverses a distance equal to its free path. What is the probability that the same two particles will again come together and collide? An approximate answer may be obtained as follows. Around the position of each particle we describe a spherical surface of radius half the distance between the particles, i.e. equal to a length of the order of the free path. Then the probability of a second meeting is the probability that they will both be at the point of contact of two spherical surfaces on a sector of the order of πd^2. The probability of one particle arriving there (if all directions of motion are equally probable) is $\pi d^2/4\pi\lambda^2$, and the same applies to the second particle. Thus the resultant probability is $(d^2/4\lambda^2)^2$. If the distance between the particles is less than twice the free path, the probability of meeting will be more than this value. The probability of a second meeting is thus very small, less than 10^{-10}. This is not surprising. If it is considered that the total number of collisions per second in 1 cm^3 of gas is $\sim \pi d^2 u n^2$ (where d is the diameter of the molecule, u is the average velocity, and n the number of molecules in unit volume), and the number of binary combinations of n particles is $n(n-1)/2 \cong n^2/2$, the probability of a collision per second of any one definite pair is $2\pi d^2 u$, i.e, $\sim 10^{-10}$. Thus in a gas the probability of a second meeting of two radicals which have just been formed is negligibly small.

The position is quite different in solutions. The kinetics of reactions in solutions have been reviewed by one of us[125]; part of this work is given below.

In gases the molecules collide once in one combination and then fly apart to collide with others in other pairs. In a solution with a coefficient of diffusion $D \cong 10^{-5}$, the length of elementary displacement of a molecule is $\sim 10^{-11}$ cm, i.e. considerably less than the molecular diameter. Two colliding molecules are surrounded by a tight ring of solvent, so that the collision is repeated many times with the same pair, until finally one of the particles manages to break through the surrounding solvent to a distance of the order of 3×10^{-8} cm, i.e. much greater than the length of a single elementary displacement. A molecule of solvent will then wedge between the two molecules and they will have become separated. This picture of repeated collisions is specific for solutions.

The total number of binary collisions of molecules of one sort in the solution is given by the formula

$$S = \frac{c^2 n^2}{6ND},$$

* A recent paper[123] has presented data favouring a mechanism in which in the decomposition of t-butyl per-esters there is simultaneous cleavage of $C-C$ and $O-O$ bonds with the formation of a molecule of CO_2 and t-butoxy and alkyl radicals in a single act. An analogous mechanism is probably also possible in the case of δ-phenylvaleryl peroxide[124].

where n is the number of dissolved molecules of the given sort in unit volume, N is the total number of molecules in unit volume, D the coefficient of diffusion, and c the velocity of the molecules.

This number of collisions includes all repeated collisions, each of which is treated by this formula as a new act. It is important for us to know the number of collisions of the "second type", i.e. the number of collisions of two particles from the time of their approach until they are separated by the solvent. For this we must know the number of collisions which one molecule experiences in unit time, and the period of time for which two molecules of one sort are together.

From the fundamental equation for unidimensional diffusion,

$$\frac{du}{dt} = D\frac{d^2u}{dx^2},$$

it follows that the probability of finding a particle at time t in the interval from x to $x + dx$, if at zero time it is at the origin, is

$$\omega(x)dx = \frac{1}{\sqrt{4\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right)dx.$$

Hence the probability of radical displacement is

$$\omega(r)dr = \frac{4\pi}{(4\pi Dt)^{3/2}}\exp\left(-\frac{r^2}{4Dt}\right)r^2dr.$$

The average radical displacement in time t is

$$\bar{r} = \int \frac{4\pi}{(4\pi Dt)^{3/2}}\exp\left(-\frac{r^2}{4Dt}\right)r^3dr.$$

The most probable displacement in time t is

$$r = \sqrt{4Dt}\,.$$

It may be assumed that the repeated collisions of one pair will continue until the displacement has reached a certain value of r, i.e. until a solvent molecule comes between the colliding pair. This time will be

$$t = \frac{r^2}{4D}.$$

The solution may be considered as an aggregate of fairly densely packed molecules. If an instantaneous picture is taken of the solution, there would be a certain number of binaries. The probability that a molecule of solute taken at random will be a member of a pair is $n - 1/N - 1$. Hence the total number of pairs is

$$\frac{(n-1)n}{2(N-1)} \cong \frac{n^2}{2N}.$$

Each of the $n^2/2N$ binaries exists for time t as regards repeated collisions, i.e. until the pair separates. We may assume that in each $r^2/4D$ sec, $n^2/2N$ new binaries will be formed. Thus we obtain for the number of primary collisions, without considering repeated collisions,

$$S' = \frac{2n^2D}{Nr^2}.$$

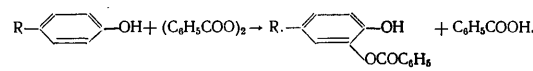
Calculation shows that a meeting with a new molecule takes place on an average approximately within 10^{-8} sec. Moreover, from the formula for S each collision is repeated within $\sim 3 \times 10^{-11}$ sec. This means that once having collided, the molecule in a given pair will continue to collide repeatedly several hundred times, until a solvent molecule comes between them and breaks up the pair. In our calculations we have assumed normal conditions and have shown only the orders of the values.

The above considerations apply in full measure not only to colliding molecules, but also to radicals and atoms formed in the thermal or photochemical decomposition of molecules. If the particles formed in these processes do not possess sufficient excess energy to allow them to break through the "wall" of solvent, they continue to collide repeatedly with each other and with the surrounding solvent molecules. This may lead to the formation of new bonds between them, to disproportionation, etc., before one of the particles is able to react with any other dissolved molecule. This explains, in particular, why some ethane was formed in the experiments of Szwarc and coworkers in isooctane solution, even in the presence of iodine and p-benzoquinone, which react rapidly with free radicals.

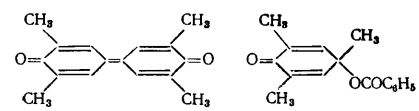
This effect of the possible reaction of two radicals or molecular fragments during the time when they are held in a "cage", i.e. surrounded by solvent without being able to separate, is the "cage" effect, which is of importance in the mechanisms of certain reactions in solutions.

6. THE OXIDATION OF PHENOLS WITH ACYL PEROXIDES

When benzoyl peroxide reacts with phenols unsubstituted in the *ortho*-position, the reaction products are mainly the monobenzoates of the corresponding pyrocatechols[126]:



Under these conditions 2,6-dimethylphenol is converted to 3,3',5,5'-tetramethyl diphenoquinone (LXIII); 2,4,6-trimethylphenol gives mainly 2,4,6-trimethyl-4-benzoyloxycyclohexa-2,5-dienone (LXIV):



(LXIII) (LXIV)

Similar results were obtained in the oxidation of cresols with acetyl peroxide in acetic acid[127].

The rate of the reaction between various phenols and benzoyl peroxide follows an equation of the second order (first order with respect to phenol concentration and first order with respect to benzoyl peroxide)[128]. The reaction of *ortho*-substituted phenols is somewhat slower than in the case of *para*-substituted phenols. In a solution of 2,6-di-t-butylphenol at 30° no reaction at all is observed. Electron donating substituents (OCH_3, CH_3) in the *para*-position accelerate the reaction. Phenols containing electron withdrawing substituents (p-Cl, p-Br) react somewhat more rapidly than unsubstituted phenol, but more slowly than p-cresol and p-anisole.

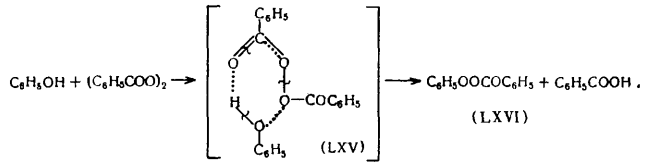
The reaction is not catalysed by acids or bases. The rate of reaction depends in a complex manner on the nature of the solvent. Increase in the polarity of the solvent causes an increased rate of reaction. Apparently a substantial part is also played by the presence of hydrogen bonding between the solvent and the phenol, such bonding probably causing a reduction in the rate.

O-Deuterated phenols react with benzoyl peroxide at a rate which is 1.32 times slower than the non-deuterated. The magnitude of the isotope effect is independent of the structure of the phenol and remains unchanged on passing from benzoyl to acetyl peroxide; CO_2 is not given off in either case[128,130,131]. Oxygen, which is a strong inhibitor of the decomposition of benzoyl peroxide in alcohols and ethers, has almost no influence on the rate of decomposition of benzoyl peroxide in solutions of phenols[132]. The rate of reaction of *p*-methoxyphenol with various peroxide compounds in benzene is greatly dependent on the structure of the peroxide[128], the changes of rate not following the order in which the rate of thermal decomposition of the peroxides changes. In this connection it is interesting that the activation energy for the oxidation of *m*-cresol and *p*-methoxyphenol in benzene with benzoyl peroxide (17.4 and 15.3 kcal/mole respectively) is approximately half the activation energy for the thermal unimolecular decomposition of benzoyl peroxide in the same solvent[49].

Iodine and methyl methacrylate do not affect the rate of oxidation of phenols. In phenolic solutions of benzoyl peroxide styrene undergoes only thermal polymerisation[129]. The radical-initiated polymerisation of styrene in solutions of acetyl peroxide at 60°, like the evolution of CO_2 from these solutions, is greatly inhibited by the addition of 0.1 mole of *m*-cresol per litre; moreover, the rate of polymerisation of styrene initiated by azodiisobutyronitrile is slightly reduced in the presence of *m*-cresol[128].

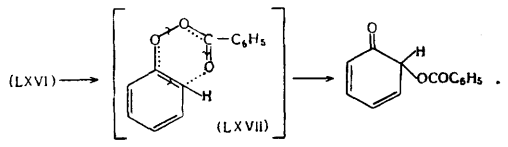
It is difficult to explain all the above facts if it is assumed[126,130,131] that free radicals take part in the oxidation of phenols. We consider it also unlikely that the radicals formed in the decomposition of the peroxide will rapidly form a complex with the phenol[133-135]. Apparently, such a reaction mechanism can be reconciled neither with the kinetic first-order reaction with respect to the phenol (since the dissociation of the peroxide into radicals would probably in this case limit the process), nor with the hydroxyl isotope effect in the phenol, or other data.

To explain the observed features of this reaction, a mechanism has been proposed[128] according to which the benzoyl peroxide and phenol react in the first and slowest stage of the reaction to form the transition state (LXV):



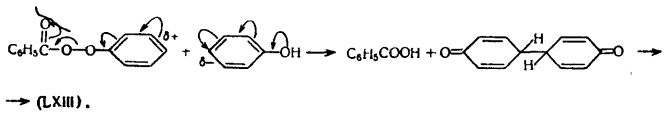
The negative entropy of activation (-26.7 e.u. for *m*-cresol, -22.3 e.u. for *p*-methoxyphenol) is in agreement with this mechanism.

The phenyl perbenzoate (LXVI) formed in the first stage rapidly isomerises by way of the cyclic activated complex (LXVII), similar to that formed in the Claisen *ortho*-rearrangement:



The resulting 2-benzoyloxycyclohexa-3,5-dienone then either undergoes prototropic rearrangement to form pyrocatechol monobenzoate, or is converted by anionotropic rearrangement to the benzoyloxydienone, as in the case of 2,4,6-trisubstituted phenols. Both these rearrangements probably also involve cyclic activated complexes.

The presence of the partial positive charge in the *para*-position of the phenyl group of phenyl perbenzoate enables compounds of type (LXIII) to be formed:



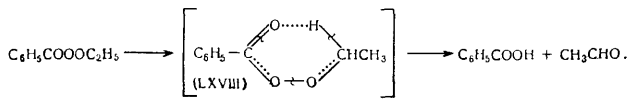
→ (LXIII).

It may be thought that the formation of esters of per-acids by way of (LXV) takes place by the reaction of acyl peroxides with alcohols[132,136-139], as well as by other reactions. The high yield of the acid corresponding to the acyl group obtained in these experiments (usually more than 1 mole of acid per mole of peroxide) supports this suggestion. In the thermal decomposition of acyl peroxides the yield of acid is usually low; thus, for example, acetyl peroxide in isooctane or cyclohexane gives mainly methane, ethane, and CO_2.

The reaction of acetyl benzoyl peroxide with alcohols[140,141] is of great interest in this respect. Because of the asymmetrical structure of the peroxide, the O—O bond is probably polar, the oxygen attached to the benzoyl group carrying a partial negative charge. This is apparently the reason why, in its reaction with methyl, ethyl, isopropyl and n-butyl alcohols, the yield of benzoic acid is ~1 mole per mole of initial peroxide.

Depending on its structure, the resulting per-ester can react by an intramolecular or a radical mechanism.

The main decomposition products of benzoyl peroxide in ethyl alcohol are acetaldehyde and benzoic acid[137]. This can be explained by the decomposition of the intermediate ethyl perbenzoate as follows:



The radical-chain decomposition of peroxidic compounds in such systems is inhibited by the addition of α,α-diphenyl-β-picrylhydrazyl[142]; for example, in the presence of α,α-diphenyl-β-picrylhydrazyl, the active-oxygen concentration in a solution of acetyl benzoyl peroxide in isopropyl alcohol at 45° is constant over a period of 120 min, i.e. a time sufficient for 80% reaction in the absence of the inhibitor[141]. Thus for isopropyl alcohol the radical-chain mechanism predominates over the intramolecular reaction. However, in solutions of methyl alcohol in the presence of α,α-diphenyl-β-picrylhydrazyl, only processes connected with gas-formation are inhibited; benzoic and acetic acids have been separated from the reaction products. Probably in the case of methyl alcohol the intramolecular reaction with a transition state of type (LXVIII) is more rapid than in the case of isopropyl alcohol.

It is interesting that the decomposition of acetyl peroxide in primary and secondary alcohols apparently takes place mainly by a radical mechanism[143]. This difference between acetyl peroxide and benzoyl peroxide[137] can be explained by the probably greater ease of formation of the perbenzoate, and also by the reduction of the energy of the transition

state (LXVIII) because of conjugation of the phenyl group with the activated complex. Consequently, the intramolecular reaction with acetyl peroxide requires a greater activation energy than for benzoyl peroxide.

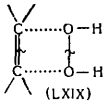
t-Butyl per-esters decompose mainly with the formation of free radicals[123]. This is probably because the formation of the cyclic activated complex of type (LXVIII) is here hindered.

In addition to radical and intramolecular reactions of the per-ester in the system acyl peroxide–alcohol, decomposition of the acyl peroxide itself is thus also possible. The relative parts played by intramolecular and radical processes are altered as the temperature is changed, which probably explains the increased yield of CO_2 at increased temperatures in the decomposition of benzoyl peroxide[138] and acetyl benzoyl peroxide[140,141] in alcohols.

7. THE OXIDATION OF OLEFINES

Depending on the conditions, the reaction of hydrogen peroxide with olefines can give various products. There is usually no reaction if olefines are brought into contact with dilute hydrogen peroxide for several days in the dark in the absence of catalysts, but irradiation with a mercury lamp of solutions of allyl alcohol, crotonic or maleic acid, or diethyl maleate in 5–10% hydrogen peroxide for 20–30 h causes addition of H_2O_2 across the double bond[144].

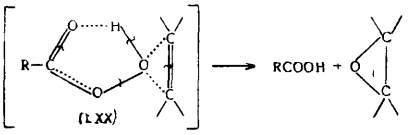
Apart from addition reactions, the hydrogen peroxide decomposes into water and oxygen, and side oxidation reactions take place when the olefinic molecule contains carboxyl or other functional groups. In spite of the extremely favourable conditions for the development of radical mechanisms for the addition to the double bond, such reactions apparently did not occur under the conditions studied[144]. Thus when maleic acid and diethyl maleate are oxidised, the products are mesotartaric acid and its diethyl ester, corresponding to *cis*-addition of H_2O_2 to the olefine. For a radical mechanism, the formation of mixed products or even predominantly the product of *trans*-addition would be expected. For an explanation of the mechanism of this reaction, it is natural to consider the formation of the four-membered cyclic transition complex (LXIX), which is made up of a photo-activated hydrogen peroxide molecule and an olefine molecule:


(LXIX)

The OH· radicals also formed under the reaction conditions cause the decomposition of the hydrogen peroxide into water and oxygen. The radicals also participate in various side oxidations, but probably do not take part in addition reactions*.

In sulphuric-acid solutions, certain olefines add on hydrogen peroxide to form the corresponding hydroperoxides[89,90,146]. The reaction is probably analogous to the acid-catalysed hydration of olefines.

When olefines react with per-acids, epoxides are formed (the Prilezhaev reaction[147]). Numerous investigations[148] have shown that reaction occurs easily in non-polar media. The reaction is of second order[149,150] (first order in respect of olefine and of per-acid). The velocity constant remains unchanged if the initial per-acid concentration is altered and if small amounts of benzoic acid and mineral salts are added[150]. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the reaction of substituted stilbenes with perbenzoic acids are 13–17 kcal/mole and from -21 to -23 e.u. On passing from benzene to a more polar solvent, such as diethyl ether, the values of the enthalpy of activation ($\Delta H^{\neq}$) are slightly increased. This, and the absence of any influence by acid or mineral salts on the velocity constant, are not in agreement with the view that the reaction mechanism is ionic[10,151]. The small increase in the values of $\Delta H^{\neq}$ as the double-bond character of the $>C=C<$ bond decreases in a series of substituted styrenes favours the view that the per-acid reacts with the carbon double bond, and not with one of the carbon atoms of the ethylenic bond. The introduction of electron-accepting groups into the perbenzoic acid also slightly reduces the enthalpy of activation. The experimental data are satisfactorily explained by a mechanism involving the transition state (LXX):[152]



(LXX)

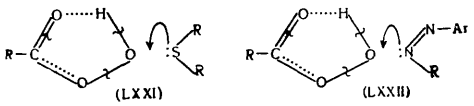
A mechanism involving such a transition state* is in agreement with the existing data on the stereospecificity of the Prilezhaev reaction[153].

It may be assumed that the oxidation with per-acids of the phenylhydrazones of substituted benzaldehydes[154], of 4,4'-dichlorodibenzylsulphide[155], and of diphenylsulphoxide[156] also takes place by an intramolecular mechanism through a transition state analogous to (LXX). All these reactions are characterised by low energies of activation (5–16 kcal/mole) and highly negative entropies of activation (from -20 to -40 e.u.). The rate of reaction and the activation parameters for the oxidation of the disulphide, olefines, and benzaldehyde phenylhydrazones are little altered on passing from benzene to diethyl ether and are independent of the presence in the solution of benzoic acid or inorganic salts. The oxidation of 4,4'-dichlorobenzylsulphide takes place 25 times as rapidly in toluene as in isopropyl alcohol, which may be explained, in accordance with mechanism (LXXI), by the destruction in this solvent of intramolecular hydrogen bonding in the per-acid. Electron-accepting substituents in the reacting molecule increase the activation energy, and in the per-acid decrease it.

* A short communication on the influence of allyl alcohol on the photochemical decomposition of hydrogen peroxide has recently appeared[145]. The authors found that the main reaction products of allyl alcohol with the peroxide under these conditions are the isomeric tetrahydroxyhexanes. These results cannot be compared with those of Milas[144], who obtained glycerol by the photochemical oxidation of allyl alcohol with hydrogen peroxide, until a more detailed account is published.

* The method of molecular orbitals gives for the system  three strongly bonding levels - 2.46 β, - 1.48 β, and - 0.618 β, one zero level, and three anti-bonding levels. This gives an energy of - 9.12 β for six and for eight electrons.

These results can be satisfactorily explained by the mechanism[155] in which the oxidation of 4,4'-dichlorobenzylsulphide passes through the transition state (LXXI):



(LXXI) (LXXII)

In the case of the disulphide, the sulphur atom, possessing an unshared pair of electrons, is the donor.

In the case of the phenylhydrazones of substituted benzaldehydes, it has been suggested[154] that there is an equilibrium,

$$C_6H_5CH=N-NH-Ar \rightleftharpoons C_6H_5CH_2-N=N-Ar,$$

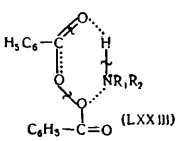
further reaction,

$$C_6H_5CH_2-N=N-Ar + C_6H_5COOH \rightarrow$$

$$\rightarrow C_6H_5CH_2-\overset{+}{N}=N-Ar + C_6H_5COO^-,$$

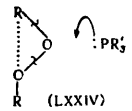
passing through the transition state (LXXII), as for disulphides. The donor is here the nitrogen atom, possessing an unshared pair of electrons, as distinct from the oxidation of olefines, where the electron donor is the molecular orbital of the multiple bond $>C=C<$. This is because in the $-N=N-$ group, the electrons of the multiple nitrogen bond occupy more stable molecular orbitals than is the case with the $>C=C<$ bond (the $>C=C<$ double bond makes a smaller contribution to the energy of the molecule than the $-N=N-$ bond; moreover, for nitrogen, unlike carbon, the π-bond is more stable than the σ-bond).

Without entering into a detailed discussion of this question, we would point out that the reaction of amines with acyl peroxides can proceed with the formation of free radicals[157] or by a non-radical mechanism[156,159], depending on the structure of the amine. For example, the reaction of benzoyl peroxide with aliphatic secondary amines to form the acid and the dialkylhydroxylamine ester has certain kinetic features which are difficult to explain by a mechanism in which radicals or ions take part. The reaction is of second order[158,159]. The rate of the reaction of diethylamine with benzoyl peroxide is unchanged on passing from dioxane to acetone, is slightly reduced in benzene, and is further reduced in diethyl ether[159]. Solutions of benzoyl peroxide with diethyl-, dipropyl-, di-n--butyl- and diisobutylamines, as distinct from solutions of aromatic amines with benzoyl peroxide in benzene and acetone[158,160] do not absorb oxygen or nitric oxide[159]. The rate of reaction is unchanged if the reagents are in contact with air instead of nitrogen. These results led Chaltykyan and coworkers to the conclusion[159] that the reaction of the enumerated aliphatic secondary amines with benzoyl peroxide proceeds by an ionic and not by a radical mechanism, with the intermediate formation of an amine-peroxide complex. We think it probable that in solvents such as benzene, dioxane, diethyl ether, etc., the reaction proceeds without the participation of ions by way of the cyclic activated complex (LXXIII):



(LXXIII)

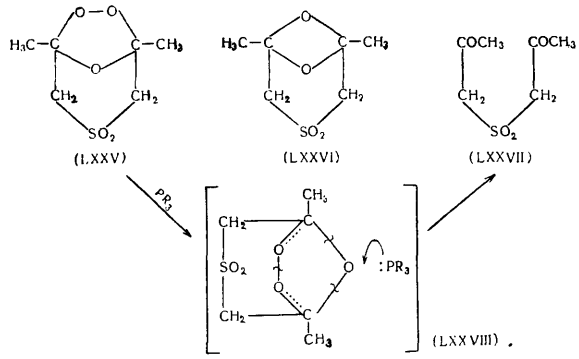
Tertiary phosphines also react with acyl peroxides, hydroperoxides and alkyl peroxides by a non-radical mechanism. From a study of the formation of triphenylphosphine oxide and acid anhydride from triphenylphosphine and acyl peroxides[161,162] it has been concluded that this reaction proceeds by the intermediate formation of ion pairs in which the anion is relatively free. Reduction of alkyl peroxides and hydroperoxides with trialkylphosphines yields the ether and the alcohol respectively[163], probably by way of the transition state (LXXIV):



(LXXIV)

During the reaction the weak peroxide bond is broken, but a stable dative bond between the phosphorus and the oxygen is formed.

The reduction of dimethylbutadiene sulphone ozonide (LXXV) is of interest[163]; the structure of (LXXV) was established by Staudinger and Criegee[164]. Instead of the expected reduction product (LXXVI), diacetonylsulphone (LXXVII) is formed[163], probably by way of the transition state (LXXVIII):

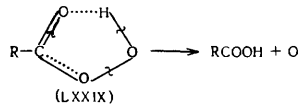


(LXXV) (LXXVI) (LXXVII)

(LXXVIII).

It is seen from (LXX), (LXXI), and (LXXII) that intramolecular hydrogen bonding in the per-acid plays a significant part in these oxidation processes[165-169]. The destruction of this hydrogen bonding in hydroxylic solvents leads to a considerable reduction in the rate of reaction, as mentioned above.

The possible decomposition of the per-acid molecule to atomic oxygen and acid is of interest:



(LXXIX)

This is clearly an endothermic reaction, with a heat change approximately equal to the energy of the O—O bond (if it is assumed that the energy due to hydrogen bonding in the per--acid and the difference in the conjugation energies of the COOOH and COOH groups compensate one another). The activation energy of this reaction should therefore be equal to or greater than the energy of the O—O bond.

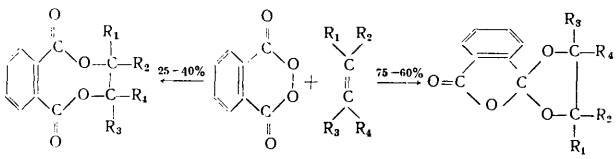
Recently, the above reaction of (LXXIX) was suggested as an explanation of the decomposition of perlauric acid into lauric acid and oxygen in benzene, methanol, acetic acid, and t-butylbenzene[170]. These authors say nothing of

the reaction of atomic oxygen with the solvents, which makes it doubtful whether this scheme can explain the observed reaction. Moreover, the existence of acid catalysis and certain other features in this reaction indicate that it proceeds by another more complex route, with the formation of molecular and not atomic oxygen. Further study of this reaction is necessary before the mechanism can be considered in more detail.

Processes involving the above decomposition of (LXXIX) probably occur in certain oxidations, particularly of aldehydes (see, for example, Knorre and Emanuel'[168]).

It has been suggested[171] that the oxidation of olefines in the presence of inorganic per-acids (pertungstic, pervanadic, etc.) proceeds analogously to the Prilezhaev reaction. From the literature on the formation of glycols in the presence of osmium tetroxide and pertungstic, permolybdic, and other inorganic per-acids, it appears that the reaction proceeds by a non-radical mechanism. In the case of OsO_4 *cis*-products are predominantly formed[172-176]; in the presence of pertungstic and permolybdic acids and selenium dioxide, *trans*-addition takes place[172], as in the bromination of olefines. These differences in the action of inorganic per-acids makes it doubtful whether a single mechanism exists for the oxidation of olefines by their action. A detailed discussion of this question is outside the scope of this article.

The recently studied reaction of phthaloyl peroxide (LXXX) with olefines is of interest[177,178]; cyclic phthalates (LXXXI) and lactones (LXXXII) are formed. Study of the reaction products of *cis*- and *trans*-stilbenes has shown that the addition is very stereospecific:



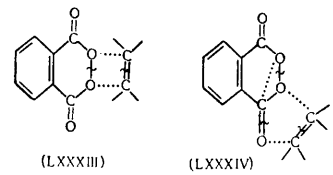
(LXXXI) (LXXX) (LXXXII)

At 20°–80° in CCl_4 the reaction is of second order in the conversion range 0–90% for all the olefines studied[177,178]. As in the oxidation of olefines with per-acids, the presence of electron-donating substituents in the olefine increases the rate of reaction. For 1,1-diphenylprop-1-ene, *trans*-*p*-methoxystilbene and tetraphenylethylene the enthalpy of activation is from 11.6 to 14.5 kcal/mole, and the entropy of activation about -27 e.u.

The second order reaction, the low activation energy, and the stereospecificity of the reaction are difficult to explain on the assumption that addition of phthaloyl peroxide to the olefine is preceded by the isomerisation of the peroxide to a biradical. Considering the second order reaction over a wide range, such an assumption[177,178] would require the sum of the heat change of the isomerisation step and the activation energy for the addition of the biradical to the olefine to be 11.6–14.5 kcal/mole (the observed activation energy), which is not very probable. Green and Rees[178] also concluded that the reaction proceeds without the participation of free radicals, after comparing the relative rates of reaction of various olefines with phthaloyl peroxide, perbenzoic acid, bromine, and the trichloromethyl radical.

It is not very probable, but not impossible, that ion pairs take part in this reaction[178]. Comparison of the activation parameters for this reaction in CCl_4 with the values of $\Delta H^{\neq}$ and ΔS for the reactions of per-acids with azo compounds[154], olefines[155], and sulphoxides[156] considered above shows that all these reactions have a low activation energy and a low entropy of activation (from -20 to -40 e.u.). The presence of ions or ion pairs, as indicated above, does not agree with the experimental data on the kinetics of the reaction of per-acids with unsaturated compounds and compounds possessing unshared pairs of electrons. The same is apparently true for the reaction of phthaloyl peroxide with olefines.

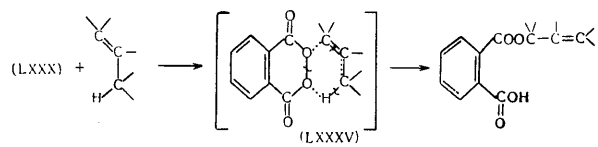
Cyclic phthalates may be formed by way of the transition state (LXXXIII), and lactones by way of the six-membered activated complex (LXXXIV):



(LXXXIII) (LXXXIV)

The distortion of the angles in the original peroxide facilitates the formation of the six-membered ring in (LXXXIV).

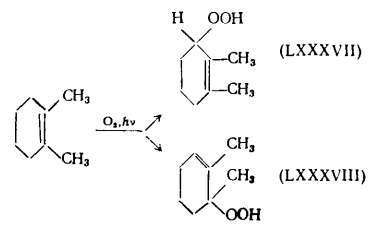
When the olefine contains an α-hydrogen atom, the reaction is more complex, because of the formation of an acid phthalate in addition to the cyclic phthalate and the lactone[178]. This reaction probably proceeds as follows:



(LXXXV)

For example, cyclohexene produces 2-cyclohexenyl acid phthalate. Separate experiments showed that the cyclohexene cyclic phthalate and lactone are completely stable under the reaction conditions, and are not intermediates in the formation of the acid phthalate.

The formation of acid phthalates by the reaction of phthaloyl peroxide with certain olefines is similar to the auto-oxidation of olefines[179,180], which is also accompanied by the migration of the double bond. Apparently, in many cases this reaction proceeds by splitting off the α-hydrogen atom to form a free radical of the allyl type: $-C_1-\dot{C}_2-\dot{C}_3-$. Recombination of this radical with the peroxide radical yields a hydroperoxide in which the peroxide group is attached to one of the carbon atoms formerly forming part of the double bond, or to the α-carbon atom. For example, the oxidation of 1,2-dimethylcyclohexene (LXXXVI) gives the isomeric peroxides (LXXXVII) and (LXXXVIII):[180]



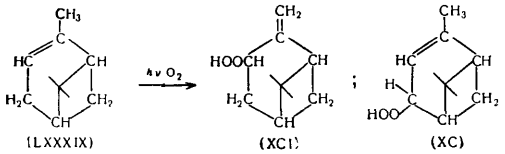
(LXXXVII) (LXXXVIII)

(LXXXVI)

The relative yields of the oxidation products clearly depend on the electron-density distribution in the free radical.

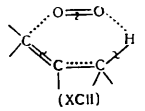
However, the photo-sensitised oxidation almost exclusively produces hydroperoxides in which the double bond has migrated, as many experiments by Schenk and coworkers have shown[181]. Such an exceptionally smooth reaction (yields

80–90% of theory) is difficult to explain merely by electronic effects in the free radical. For example, α-pinene (LXXXIX) would be expected to form a free radical by splitting off the hydrogen atom attached to a secondary carbon atom; in fact the auto-oxidation of α-pinene proceeds through the formation of the hydroperoxide (XC), while in the photo-sensitised oxidation the hydroperoxide (XCI) is formed in 80% yield:



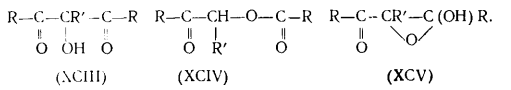
(LXXXIX) (XCI) (XC)

The reaction probably proceeds by way of the photo-activated cyclic transition complex (XCII), analogous to that suggested for the phthaloyl peroxide reaction:



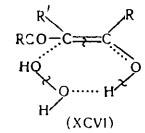
(XCII)

Enolisable β-diketones are easily split by per-acids[182–187], the main reaction products when the reactants are taken in equivalent quantities being an α-hydroxy-β-diketone (XCIII) and an ester of a ketoalcohol and an acid (XCIV). The ester (XCIV) is apparently formed by the thermal or base-catalysed rearrangement of the α-hydroxy-β-diketone[183,187] or of the isomeric epoxide (XCV):[186]



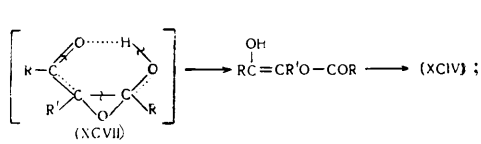
(XCIII) (XCIV) (XCV)

The first step is probably the reaction of the enolised β-diketone with the per-acid. House and Gannon[186] consider that this reaction can form either the epoxide (XCV) or the hydroxydiketone (XCIII) by way of (XCVI):



(XCVI)

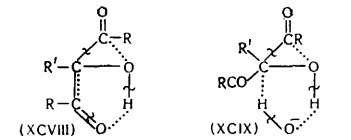
They suggest that the ester (XCIV) forms as a result of the thermal rearrangement of the epoxide (XCV) by way of the transition state (XCVII):



(XCVII) (XCIV);

or by the action of a base through an intermediate carbanion.

The formation of an epoxide by the reaction of an enolised diketone with a per-acid under the mild conditions in which the reaction is carried out appears improbable. For example, α,β-unsaturated acids are oxidised with difficulty by per-acids, but at increased temperatures give mainly hydroxy compounds[149]. With per-acids, α,β-unsaturated ketones usually undergo the Bayer–Villiger reaction[182,188–190]. It is possible that the only product of the reaction of the enolised diketone with the per-acid is a hydroxydiketone. The ester may be formed by the thermal rearrangement of the hydroxydiketone by way of (XCVIII):

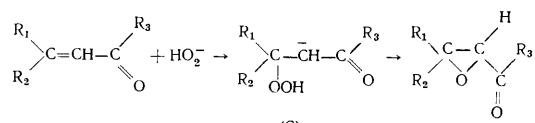


(XCVIII) (XCIX);

or by the action of bases by way of the transition state (XCIX). The question of the competition of mechanisms in which the epoxide and hydroxydiketone take part requires further studies, first and foremost of the tautomeric equilibrium between these compounds.

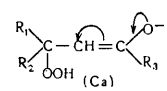
In aqueous or alcoholic alkaline solutions, where radical reactions do not usually occur, hydrogen peroxide does not react with hydrocarbons containing an isolated double bond or a double bond in conjugation with a group other than a carbonyl or nitrile group. α,β-Unsaturated nitriles and carbonyl compounds, including certain quinones[191,192], form the corresponding epoxides. Weitz and Scheffer[193] were the first to study this reaction, using α,β-unsaturated ketones. It has recently been shown[194] that α,β-unsaturated ketones can be converted to epoxides in benzene solutions by means of t-butyl peroxide in the presence of small quantities of benzyltrimethylammonium hydroxide. The catalyst is added to the benzene solution as a 36% solution in methanol.

The kinetic study of the hydrogen peroxide oxidation of mesityl oxide and ethylideneacetone in alkaline solution has shown that the rate of reaction is proportional to the concentrations of the HO_2^- ion and olefine[195]. Bunton and Minkoff consider the reaction to pass through the intermediate formation of the carbanion (C), the rate of its formation determining the overall rate:



(C)

Apparently, the formation of an addition product of the HO_2^- ion and the double bond of the α,β-unsaturated carbonyl compound is not in general excluded, but bearing in mind existing data on the electron affinities of the carbon and oxygen atoms[196], the negative charge residing mainly on the carbonyl oxygen, we consider that the structure of the anion is more correctly given by (Ca):

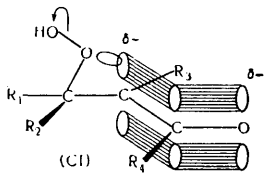


(Ca)

The formation of epoxides by the alkaline hydrogen peroxide oxidation of *cis*- and *trans*-benzalacetones[197,198], β-methyl-*trans*-benzalacetophenone and other derivatives[199,200] shows that the reaction is not stereospecific. For example, both benzalacetophenone isomers yield only the *trans*-oxide, while β-methyl-*trans*-benzalacetophenone gives a mixture of the *cis*- and *trans*-epoxides. The oxidation of *cis*- and *trans*-3-methylpent-3-en-2-one produces only 3-methyl-*trans*-3,4-epoxypentan-2-one[201].

From an analysis of the large mass of experimental material on the stereochemistry of the conversion of α,β-unsaturated ketones into epoxides and the oxidation of

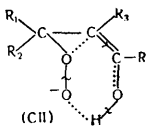
α,β-unsaturated nitriles, it has been concluded[202] that the stereochemistry of the formation of the epoxide is determined by the minimum steric hindrance to coplanarity in the group $-\overset{|\curvearrowleft}{C}=\overset{|\curvearrowleft}{C}-O-$ in the transition state of the following structure (CI):



(CI)

It is suggested that the repulsion of the group COR_4 by the groups R_3 and R_2 is the main hindrance to coplanarity. Coplanarity strengthens conjugation and reduces the activation energy, but slight distortions of the valency angles (within 20%) cannot substantially affect the energy of delocalisation of the electrons in the transition state.

The existing data on this reaction do not contradict the suggestion that the reaction passes through the cyclic activated complex (CII). The repulsion caused by the spatial distribution of the groups R_3 and R_2 must affect the activation energy.



(CII)

In the present article we have restricted ourselves to a review of a few reactions, and, of course, we have not exhausted all the various processes in which peroxides take part. Intramolecular mechanisms are found in many reactions outside those reviewed here, such as the decomposition of tertiary hydroperoxides in alkaline solutions into alcohols and oxygen, the decomposition of dialkyl peroxides containing a secondary carbon atom at the peroxide bond into acetone and alcohol under the action of amines or alkali-metal alcoholates, the oxidation of organoboron compounds, etc., many of which pass through cyclic activated complexes.

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STRAIN AND REACTIVITY IN MONOCYCLIC SYSTEMS

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INTRODUCTION

The idea of strain in cyclic molecules, as a measure of their stability and, in certain respect, their reactivity, was introduced into organic chemistry by A. Baeyer in 1885. Subsequently, Baeyer's original conceptions underwent considerable modification as a result, primarily of the new theoretical ideas, developed by Sachse and Mohr and appearing in the twenties and thirties in the work of Ružicka, Hückel, etc.

The last 10–15 years have witnessed a new stage in the development of the strain theory. A vast quantity of experimental material has accumulated by the widespread use of modern methods in organic chemistry, which provide thermochemical values to a hitherto unattainable degree of accuracy, and reliable spectral and kinetic data. These data are now of paramount importance in interpreting the physical properties and chemical behaviour of cyclic molecules. Strain cannot now be regarded as a function only of the deformation of the valence angle; other types of strain can be distinguished, which are sometimes of greater importance in determining the properties of cyclic compounds. A characteristic feature of many recent chemical investigations of ring strain is that they reflect the influence of strain on chemical properties not related to the rupture or

formation of rings. This permitted a fresh approach to the evaluation and explanation of the phenomenon of strain.

It is not possible in this paper to encompass the whole mass of physical, thermochemical and chemical data connected with the history and the present state of the strain theory. For this reason, the authors, while appreciating the possibility of serious omissions, have decided to confine themselves to a consideration of what they believe to be the more interesting recent work, with only a short preface reviewing the development of the fundamental tenets of the strain theory up to the 1940's*. More comprehensive reviews of the evolution of the theory may be found in the works of Hückel[1] and Domnin[2,3].

In the first of his works devoted to strain in cyclic compounds[4], Adolf Baeyer formulated the following proposition:

"The four valencies of a carbon atom act in directions connecting the centre to the apices of a tetrahedron and form angles of 109°28' with each other. The direction of attraction can deviate, which results, however, in strain that grows with the magnitude of the deviation". Baeyer considered half the change in the angle between two bonds to be a measure of the strain.

From the outset, Baeyer realised that the theory could be verified by thermal measurements, since strain involved an increase in energy content. "Thus, for example, the heat of combustion of hexahydrobenzene should, on the earlier view, have been twice as great as that of cyclopropane; owing to the greater strain in the latter, however, it (i.e. the difference in the heats of combustion of the two compounds) should be appreciably less"[4]. Baeyer's ideas were justified by experiment (see, for example, Zubov's well-known work[5,6]), and accurate measurement of heat of combustion remains to this day the most important criterion in the study of strain in rings.

The higher energy content of a ring should, naturally, reduce its stability. Assuming that in cyclic compounds the carbon atoms lie in one plane, Baeyer concluded that a five-membered ring was the least strained (according to Baeyer, its strain was measured by the deviation of the valency bonds, equal to 0°44'). In planar six-membered and larger rings, in which the valency angle must be greater than the tetrahedral angle, the deviation of the valency bonds becomes negative**. Thus the strain in a ring increases with ring size (for a six-membered ring, the deviation is -5°16', while for a 17-membered ring the absolute value of this deviation is equal to that for cyclopropane). When Baeyer's theory was formulated, compounds containing more than seven atoms in a ring were unknown and it was considered that they could not, in general, exist, owing to the great strain involved. At the same time, as Baeyer himself indicated, there was sufficient evidence to show that, in spite of its greater strain, a six-membered ring was about as stable as a five-membered ring. In 1890, Sachse[7] showed that Baeyer's conception of a planar structure for all rings was not in any way a consequence of the tetrahedral model for a carbon atom. Furthermore, if one considered that a tetrahedral arrangement of bonds was the most advantageous, a model for any ring could be constructed, with a minimum deviation from the tetrahedral angles. Such a model would not, in general, be planar. In this way Sachse showed that Bayer's conception of a planar structure was valid only for three-, four-, and five-membered rings but not for larger rings. According to Sachse, a five-membered ring was more strained than a six-membered one, for which two "normal" (i.e. unstrained) forms were possible; he called these symmetrical and unsymmetrical (corresponding to the so-called "chair" and "boat" forms). The form in which a cyclohexane derivative existed depended, according to Sachse, on the origin and nature of the substituent. In particular, Sachse considered that the most probable form of cyclohexane itself was the symmetrical (chair) one, in which he distinguished between two types of hydrogen atom (axial and equatorial, in modern terminology). From this, Sachse concluded that it was possible for isomers of monosubstituted cyclohexanes to exist. Since his predictions of the number of isomers, based on a rigid model, were not confirmed, Sachse's work did not receive the attention that it undoubtedly merited.

It was only after Mohr[8] suggested that mutual transitions from "chair" to "boat" and from "chair" to its mirror image occurred easily that it became possible to explain the discrepancy between Sachse's predictions and the experimental data. Mohr examined in detail unstrained and non-planar models of larger rings as well as of cyclohexane (the idea of the non-planarity of larger rings was stated by Sachse only in general terms). After Mohr's work[8,9], which soon received experimental support, the idea of a non-planar structure and the absence of strain for cyclohexane and larger rings became generally accepted. The work of Böeseken on the stereochemistry of cyclic 1,2-diols[10] demonstrated that six- and seven-membered rings had such a structure; likewise, that of Hückel, who prepared *trans*-decahydronaphthalene[11], the existence of which had been predicted by Mohr. After Ružicka had shown that the natural perfumes — muscone and civetone — were macrocyclic ketones[12,13] and had synthesised a number of similar ketones[14], the question of whether many-membered rings could exist was finally settled. Macrocyclic compounds appeared to be perfectly stable[15], although in Baeyer's view they should have possessed about the same amount of strain as three- and four-membered rings. There was thus no doubt about the lack of strain and hence the non-planar structure of the largest rings. As the number of links increase, a many-membered ring compound approximates to a three-dimensional kind of linear "twofold" straight-chain macromolecule, the ends of which are connected by "half" of a six- or five-membered ring[16].

The Baeyer strain theory, supplemented by Sachse and Mohr provided the explanation of a large number of phenomena. However, new facts began to emerge quite soon, which could not be explained by this theory alone.

In 1930, Stoll and Stoll–Comte published a paper[17] in which they discussed the relation between ring-size and density of cyclic hydrocarbons. They noticed that hydrocarbons of intermediate ring-size had anomalously high densities and that their preparation by Ružicka's method gave very poor yields. From a consideration of models of cyclic hydrocarbons, made up of spheres (the diameter of the van der Waals sphere for C was taken as 1.55 Å and that for H as 2.3 Å), the authors concluded that in intermediate-sized rings a compression of the van der Waals spheres for the hydrogen atoms occurred. Somewhat later, Carothers[18] developed in detail the idea that interaction between atoms attached to the carbon chain (generally hydrogen atoms)

* In this review, we have intentionally confined ourselves to monocyclic systems and have excluded polycyclic compounds. We intended in this way to simplify the presentation as far as possible and to clarify the new ideas developed in recent years.

** Occasionally, the term "negative strain" is used in connection with six-membered and larger rings.

was the cause of interference in ring closure and of strain in already formed rings. The effective volume of the hydrogen atom used by Stoll was clearly too high, so that the idea of compression cannot be considered as substantiated. Nevertheless, the idea that interaction between atoms not directly bonded is responsible for strain, has proved extremely fruitful.

In a cyclic system, two types of interaction between atoms not directly bonded are possible: (1) transannular (across the ring, i.e. 1,3-, 1,4-, 1,5-, and 1,6-interactions); (2) vicinal, i.e. between substituents on neighbouring atoms of the ring. Those peculiarities in properties that depend on a transannular effect are more clearly manifested in compounds with an intermediate-sized ring (8–12 members), a fact that is connected with the peculiar geometry of these compounds (for greater detail, see the review by Gol'dfarb and Belen'kii[19]).

We shall consider here certain cases of the second type of interaction which depends mainly on the volume of the substituents, i.e. on purely steric factors, similar to those responsible for restricted rotation about single bonds.

Let us briefly consider the internal rotation* of a molecule of n-butane about the single C–C bond between the second and third carbon atoms. During such rotation, the butane molecule is continuously changing, forming an innumerable number of conformations**. Of these, we shall select six extreme ones. The curve in Fig. 1 shows the relation between potential energy and angle of rotation; the six conformations correspond to the maxima (eclipsed forms) and minima (staggered forms).

The difference of energy between the most favourable conformation, *d*, and the unfavourable conformations, *a* and *c* is 4 and ~3.5 kcal/mole respectively (approximate data[25]). The *gauche*-conformation *b* differs from the *trans*--conformation by only 0.8 kcal/mole.[25] From this, it is understandable why an actual molecule of n-butane (and other n-alkanes) exists almost exclusively in the staggered (*trans*- and *gauche*-) conformations.

Consideration of models of cyclic compounds, in particular cycloalkanes, shows that only for cyclohexane and for macrocyclic compounds containing more than 12 atoms in a ring is it possible to construct a molecule without energetically unfavourable eclipsed conformations[26,27]. In planar, four- and five-membered rings, as was assumed in classical stereochemistry, the carbon chain must be made up of unfavourable *cis*-conformations *a*. Just this explains why 4- and 5-membered rings are not, in fact, planar. In the "chair" form of a cyclohexane molecule, all six C–C

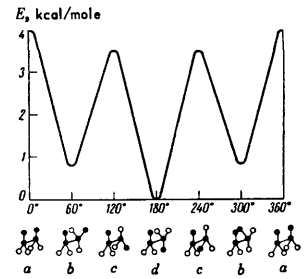


Fig. 1. Change in potential energy during the internal rotation of a n-butane molecule: *a*) cisoid conformation; *b*) skew-staggered or *gauche*-conformation; *c*) eclipsed skew conformation; *d*) transoid conformation.

bonds are in favourable, staggered conformations (the hydrogen atoms on neighbouring carbons do not face each other); in the "boat" form on the other hand, two of the six bonds are in the unfavourable conformation *a*. It is thus clear why the "chair" form of cyclohexane predominates over the "boat" form.

Seven-membered and intermediate-sized rings are energetically less favoured than six-membered ones. In the "chair" form of a cyclohexane molecule, six C–H bonds are parallel to the axis of the molecule (axial bonds), which results in a minimum interaction of axial hydrogen atoms. As the number of atoms in the ring is increased, while preserving the zig-zag form of the chain, made up of *b*-conformations, the "quasi-axial" hydrogen atoms must be displaced more and more towards the centre of the ring. However, study of models which take both covalent and van der Waal's radii into account, e.g. Stuart models, shows that only with large rings (13 links and greater) is the space inside the ring large enough to accommodate the hydrogen atoms freely, in such a way that the polymethylene chain does not contain energetically unfavourable eclipsed conformations. In this respect, macrocyclic molecules remind one of the corresponding acyclic molecules referred to earlier. In intermediate-sized rings the internal space is insufficient to accommodate all the quasi-axial hydrogen atoms while preserving the most favourable conformation of the chain. The result can be either a compression of the van der Waals radii of the hydrogen atoms and a retention of the zig-zag chain made up of *gauche*-conformations, or an alteration in the form of the chain, with the appearance of unfavourable eclipsed *c*-conformations. It is difficult to say, at present, which of these alternatives in fact happens. It is extremely probable that both can occur simultaneously. For the sake of simplicity, we shall later confine ourselves to a consideration of chain conformation as the fundamental cause of peculiarities* in chemical and physical properties

* The internal rotation of molecules has been discussed in detail in a number of reviews[20,21] and monographs[22,23] and also in the second volume of the fifth edition of A. E. Chichibabin's "Fundamental Principles of Organic Chemistry". We shall deal with this question for the sake of completeness and also to define more precisely the terms used, since, unfortunately, there is so far no generally accepted terminology in this field.

** The term "conformations" denotes those different spatial arrangements of atoms in a simple classical organic structure (configuration) that are produced by rotation or bending (but not breaking) of bonds. This definition, taken from Klyne[24], seems to us to be quite satisfactory. To avoid misunderstanding it should be emphasised that one can speak not only of a conformation of a whole molecule (e.g. the "chair" and "boat" forms of cyclohexane) but of a conformation of part of a molecule (usually, two atoms in the main chain, linked by a single bond, and their substituents).

* In particular, unfavourable conformations result in a decrease of molecular volume, which shows itself in intermediate-sized rings by an increase of density and a lowering of molar refraction. These phenomena have been particularly carefully and clearly studied for those cycloalkyl acetates which are liquid at ordinary temperatures[27].

of intermediate-sized rings. It should be noted that, apart from the compression of the van der Waals radii, the mutual approach of the quasi-axial hydrogen atoms must strengthen their interaction and therefore increase the energy content of the molecule. Consequently, one can say that both factors (interaction of the quasi-axial hydrogen atoms, i.e. transannular interaction, on the one hand and unfavourable chain conformation, i.e. vicinal 1,2-interaction, on the other) bring about an increased energy content in the intermediate-sized rings — in other words, "non-classical", conformational strain** [26,28]. What has been said above is well illustrated by the Stuart models of cyclopentane, cyclohexane, and cyclodecane (Fig. 2).

Thus, on the basis of information obtained in recent years, one can state that in addition to classical angular or Baeyer strain ("the energy increment of a compound due to deformation of the optimal valency angles" [30]), a so-called conformational strain ("that part of the energy of a compound connected with the presence of an energetically unfavourable conformation" [30]) can also be detected in cyclic systems. It should be borne in mind that, as a rule, both types of strain are present simultaneously in an actual molecule, in a state of close interaction. Thus, a cyclopentane molecule, which on the classical view is almost unstrained, proves, owing to conformational strain, to be non-planar and the non-planarity in turn results in (more accurately, it increases) angular strain.

If one assumes that the strain energy (U_{str}) of a molecule is equal to the sum of the energy of deformation of the valency angles (U_{ang}) and the energy of repulsion of the unbonded atoms (U_{rep}), it can be said that for a strained molecule, neither of the terms on the right-hand side of the equation

$$U_{str} = U_{ang} + U_{rep}$$

is equal to zero. Obviously, a real molecule will exist principally in the conformation that corresponds to the least strain energy. Physical and chemical methods, by means of which strain in rings can be detected, only give an idea of the total strain. It can only be supposed that Baeyer angular strain predominates in small rings, and conformational strain in five-membered and intermediate-sized rings.

1. PHYSICAL PROPERTIES OF CYCLIC MOLECULES AS A MEASURE OF THEIR STRAIN

Strain in rings is frequently detected by a study of certain physical properties. The determination of thermodynamic quantities, particularly enthalpy and entropy, gives valuable information, and direct determination of the geometry of a molecule by electron diffraction is also of importance. Accurate measurement of heats of combustion (Table 1) shows the presence of strain particularly clearly.

Cyclopentane and cyclohexane have been the most fully investigated, by a variety of methods. We shall therefore begin our account with these two cycloalkanes.

Electron diffraction has shown that cyclohexane normally exists in the "chair" form [41], in which the carbon chain is made up of *gauche*-conformations *b*; this is therefore more favourable than the "boat" form*. The values of the entropy and heat capacity (at constant volume) and the infra-red and Raman-spectral frequencies calculated for a "chair" model (symmetry group D_{3d}) agree well with the experimental values [42]. The heat of combustion of cyclohexane also points to the absence of strain in this compound. When calculated per CH_2 group, it is the same as that for saturated acyclic hydrocarbons. In discussing the various properties of cyclic systems related to strain, cyclohexane derivatives are used for comparison, as compounds known to be unstrained.

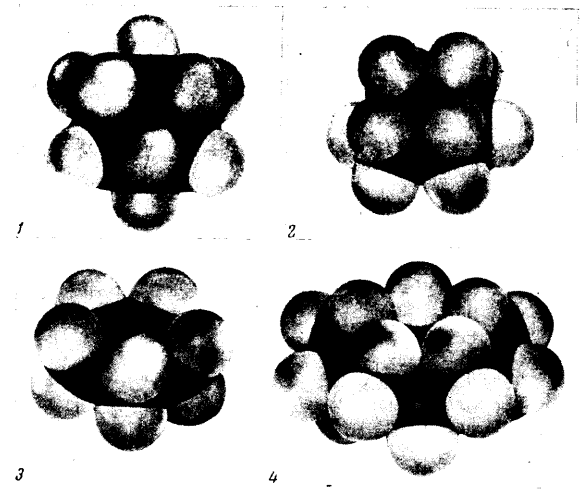


Fig. 2. 1) "Chair" form of cyclohexane; 6 axial C-H bonds parallel to the axis of the molecule, 6 equatorial hydrogen atoms arranged around the periphery; the chain is constructed of *gauche*-conformations (*b* in Fig. 1). 2) "Boat" form of cyclohexane, the chain contains 4 gauche conformations and 2 eclipsed cisoid conformations (*a*, in Fig. 1). 3) Cyclopentane (planar model); all ten hydrogen atoms are turned outwards; the chain consists of eclipsed cisoid conformations (*a*, in Fig. 1). 4) Cyclodecane (the carbon atoms lie in different planes; some of the 20 hydrogen atoms are concentrated inside the ring; the chain contains eclipsed skew conformation (*c*, in Fig. 1).

On the subject of cyclohexane stereochemistry we shall, in this review, limit ourselves to what has been said above. More detailed information may be found in numerous reviews (see, for example, ref. 43).

Cyclopentane, as has already been indicated, was for a long time thought to be unstrained. However, about 20 years ago, data emerged that entailed a reconsideration of this question. Measurements of the heats of hydrogenation of cyclopentene and cyclohexene appeared, at first sight, to be contradictory [44,45]. It might have been supposed that the

** Conformational strain is sometimes called Pitzer strain since Pitzer first compared cyclohexane and cyclopentane from this point of view [29]. In essence we are dealing here with a manifestation of steric hindrance, so that Pitzer strain can be discussed in terms relevant to this latter concept.

* The "boat" belongs to the family of so-called flexible cyclohexane conformations, which also includes the skewed or half-rotated form, discussed in recent publications (see Allinger [186] and Stolow [187] and the literature cited there).

TABLE 1. Heats of combustion of cycloparaffins.

Hydrocarbon, and the number of atoms in the ring (n)	$-\Delta H_c$ (l)	$\frac{-\Delta H_c\ (l)}{n}$	$+\Delta H_{vap}$	$-\Delta H_c$ (g)	$\frac{-\Delta H_c\ (g)}{n}$	Δ_n	$n\cdot\Delta_n$	Reference
Cyclopropane, $n=3$	—	—	—	499.85±0.13	166.6	9.2	27.6	32
Cyclobutane, $n=4$	650.22±0,10	162.5	5.56	655.78±0.16	163.9	6.5	26.0	33, 34
Cyclopentane, $n=5$	786.67±0,15	157.3	6.91	793.58±0.17	158.7	1.3	6.5	34, 35, 36
Cyclohexane, $n=6$	936.58±0,17	156.1	8.01	944.69±0.17	157.4	0	0	34, 35, 36
Cycloheptane, $n=7$	1098.9±0,15	157.0	9.42	1108.3±0.27	158.3	0.9	6.3	34, 35
Cyclooctane, $n=8$	1258.6±0,22	157.3	10.68	1269.3±0.35	158.6	1.2	9.6	34, 35
Cyclononane, $n=9$	1417.7±0,22	157.5	11.88	1429.5±0.39	158.8	1.4	12.6	34
Cyclodecane, $n=10$					158.6	1.2	12.4	37
Cycloundecane, $n=11$					158.4	1.0	10.8	37
Cyclododecane, $n=12$					157.8	0.3	3.4	37
Cyclotridecane, $n=13$					157.7	0.4	4.6	37
Cyclotetradecane, $n=14$					157.4	0.04	0.6	37
Cyclopentadecane, $n=15$					157.5	0.1	1.8	37
Cyclohexadecane, $n=16$					157.5	0.1	1.8	57

Note: $-\Delta H_c$ (l) and $-\Delta H_c$ (g) are the heats of combustion (kcal mole^{-1}) in liquid and gaseous states respectively, at 25° and constant pressure. Gaseous CO_2 and liquid H_2O are assumed to be reaction products; ΔH_{vap} is the heat of evaporation. $-\Delta H_c$ (l)/n and $-\Delta H_c$ (g)/n are the heats of combustion per CH_2 group of n-alkanes, equal to 156.26 and 157.44 kcal mole^{-1} respectively[38]. Δn is difference in the heat of combustion (in gaseous state) per CH_2 group of a given hydrocarbon and of cyclohexane (assumed to be unstrained); $n\Delta n$ is the so-called "strain", i.e. the difference between the experimental and calculated (additive) heats of combustion, assuming the increment per CH_2 group to be 157.4 kcal mole^{-1}, Old, and apparently insufficiently accurate, data on the heats of combustion of higher cycloalkanes at constant value [39,40] have not been given in the Table. However, if they are used to calculate the heats of combustion of constant pressure, good agreement with new data is obtained in a number of cases (for n = 10, 15, and 17).

conversion of a strained cyclopentene molecule to an unstrained cyclopentane molecule would be accompanied by the release of a larger amount of energy than the conversion of unstrained cyclohexene, which has a non-planar structure (for the structure of cyclohexene, see later date[46]), to cyclohexane, known to be unstrained. However, the heat of hydrogenation of cyclopentene proved, in fact, to be about 1.7 kcal/mole lower than that for cyclohexane. The explanation was found to be that cyclopentane was not unstrained[47]. Its increased energy content was attributed to the interaction of the hydrogen atoms, which, in a flat cyclopentane molecule, are in mutually eclipsing positions (conformation *a*, Figs. 1 and 2). Cohn, Kistiakowsky, and Smith[47] estimated the excess energy of cyclopentane compared to that of cyclohexane to be about 2.75 kcal per C–C bond; if one accepts the data of Dauben and Pitzer[25], this figure could be increased approximately twofold. This energy change must affect the heats of combustion, as in fact, does happen (Table 1), but it is considerably less than the values indicated for a planar model (1.3 kcal per CH_2 group, which, naturally also expresses the excess energy per C–C bond).

Aston and his colleagues obtained important data on this topic by comparing the entropy of cyclopentane, as determined by thermochemical measurements, with values calculated for various cyclopentane models: a planar model (symmetry group D_{5h}), a non-planar model with one atom outside the plane (C_s), and a non-planar model with two atoms outside the plane (C_2). The second model was found to agree best with the experimental data. The authors attributed the non-planarity of the cyclopentane molecule to mutual repulsion of the hydrogen atoms. A Raman-spectral investigation[50] also led to the conclusion that the cyclopentane molecule was probably non-planar.

After Pitzer and his colleagues[29,51] had summarised the data on electron diffraction, infra-red* and Raman spectra, and the thermodynamic functions of cyclopentane, its non-planar structure became generally accepted. The maximum deviation from planarity (referred to in the English literature as "puckering") is, in Pitzer's opinion, 0.3 Å; its

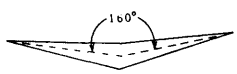
* The frequency of the infra-red absorption maximum of the carbonyl group in 5-membered cyclic ketones and lactones is appreciably higher than that in the corresponding 6-membered ring compounds. The usual explanation is that, because of the diminution of the CCC valence angle of the carbonyl group in a strained five-membered ring, the character of the hybridisation of the valence orbitals changes and causes a shift of the carbonyl absorption maximum[52]. In a recent publication[53], Hall and Zbinden tried to show that this shift depends only on a change in the character of the hybridisation, since it is also manifested by 5-membered ring compounds that, in their opinion, are unstrained; in other words, spectral data cannot indicate strain. It should be pointed out that it is not logical to consider in isolation two such closely connected factors as a change in the character of hybridisation and a diminution of the valence angle, i.e. angular strain. Hall's conclusions concerning the strain-free nature of certain 5-membered ring compounds are in error, since they are based on the inability of these compounds to polymerise. It will be shown later that no direct relation exists between strain in a ring and its tendency to polymerisation.

position is not fixed, but shifts among the five corners of the molecule. Such a shift is known as pseudo-rotation*.

Accurate measurements of heats of combustion (Table 1), have firmly established that seven-membered rings and intermediate-sized rings (8–12-membered) are strained. Similar data for macrocyclic hydrocarbons, however, clearly indicate that these are unstrained.

Further information about the presence of conformational strain in compounds containing 7-membered and intermediate-sized rings has been obtained from the heats of hydrogenation of cycloolefins in the gas phase, extrapolated to 82° (for cycloheptene and *cis*-cyclooctene)[47], and in the liquid phase at 25° (for cycloheptene[54] and the *cis*- and *trans*-isomers of cyclooctene, cyclononene, and cyclodecene[55]). All the *cis*-cycloolefins, starting from cyclohexene, and the cycloparaffins obtained from them by hydrogenation are unstrained according to the Baeyer–Sachse–Mohr conception of strain. From the point of view of classical stereochemistry, therefore, one would expect the heats of hydrogenation of *cis*-cycloolefins to be the same as those of normal *cis*-alkenes. However, this is found only for cyclohexene, whose heat of hydrogenation (28.59 kcal/mole)[47] is practically the same as that of *cis*-but-2-ene (28.57 kcal/mole)[56], and as the average value of the heat of hydrogenation of normal *cis*-olefins (28.40 ± ± 0.50 kcal/mole)**[57]. The heat of hydrogenation of cycloheptene and the other higher *cis*-cycloalkenes is lower than that of cyclohexene, which indicates that the energy content of cycloparaffins containing intermediate-sized rings is higher than that of cyclohexene and the alkenes, i.e. that the cycloparaffins are strained in the non-classical sense[55] (see the similar discussion for cyclopentane). Table 2 presents the heats of hydrogenation of *cis*-cycloolefins at 25° in acetic-acid solution with a platinum oxide catalyst[54,55].

The concept of strain in small rings has been developed somewhat in recent years. In particular, an electron-diffraction study of cyclobutane[58] showed that the four-membered ring is not quite planar, but is dihedral, with an angle of about 160° (D_{2d} symmetry). Alternatively, it could be a planar ring with low rigidity (D_{4h} symmetry) leading to large-amplitude out-of-plane bending.



This structure for cyclobutane was confirmed by comparing values of entropy obtained from experimental heat capacities and heats of transition with values calculated statistically for a planar model[59]. The observed divergence was attributed to non-planarity of the cyclobutane molecule (see the similar discussion for cyclopentane, above).

* Doubts were later expressed, based on spectroscopic studies, as to the necessity of invoking the concept of pseudo-rotation in order to explain the various properties of cyclohexane. However, new thermodynamic data indicate the validity of the original concept (see recently published work by McCullough et al[188] and the literature cited therein).

** It should be noted that the first two figures were obtained in the same experimental conditions (gas phase, 82°) while the last is for 25°. Nevertheless, it may be used for comparison, since the change with temperature of the heat of hydrogenation is less than the deviation of the calculated figures from the experimental ones (0.5 kcal/mole).

The fact that the C–C bond length in cyclobutane (1.56 Å) is somewhat greater than the normal C–C bond length, has been attributed to the mutual repulsion of unbonded carbon atoms (across the ring)[58]. It can be shown that a non-planar structure must lead to an increase of Baeyer-type strain, which is evidently compensated by a diminution of conformational strain.

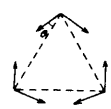
The structure of cyclopropane has been studied repeatedly, by a variety of methods. Attempts have been made to explain its high reactivity, expecially its ready isomerisation to olefins, by special features of the chemical bonds in cyclopropane compounds, as well as by the large strain of a three-membered ring.

Walsh[60] proposed the formula $CH_2{=}CH_2$ with a bond to CH_2 for cyclopropane, but it did not receive recognition. Both electron-diffraction data[61] and comparison of entropy values from thermal measurements and from a statistical method[62], lead to the conclusion that all the bonds in cyclopropane are equivalent and that the carbon atoms lie at the apices of an equilateral triangle. The vibration frequencies calculated for such a model[63] agree well with the observed values.

TABLE 2. Heats of hydrogenation of *cis*-cycloolefins.

Compound	$-\Delta H_{hydrog}$ kcal mole^{-1} at 25°
Cyclohexane	27.10±0.08
Cycloheptene	25.85±0.09
cis-Cyclooctane	22.98±0.10
cis-Cyclononene	23.62±0.07
cis-Cyclodecene	20.67±0.08

Some interesting views on the nature of the chemical bonds in cyclopropane were expressed by Coulson and Moffit[64], who proceeded from the fact that in the hybridisation of valency electrons a condition of orthogonality must be observed, i.e. the angle between the hybridised orbitals cannot be less than 90°. Since, in cyclopropane, this angle should be 60°, they proposed a special system of bent valencies ("banana" bonds). Calculation showed that the most favourable angle of deviation (θ) of orbitals from the straight line joining the carbon atoms is 22°, i.e. the angle



between the directions of the valency orbitals should be $2 \times \times 22 + 60 = 104°$. Such a concept of unusual hybridisation is, in essence, a modernised expression of the Baeyer strain theory; it enables one to explain qualitatively the high reactivity of cyclopropane compounds in reactions involving ring cleavage and also the observed shortening of the C–C bonds in cyclopropane (1.53 Å[61] instead of the usual 1.54 Å).

Dyatkina and Syrkin[66] suggested that so-called three--centred orbitals exist in cyclopropane and similar compounds. Closely similar views had been expressed earlier by Walsh[66]. Byt this means it is possible to explain both the easy rupture of a three-membered ring and the conjugation of the cyclopropane group with a double bond.

A new theory of the bonds in cyclopropane and cyclobutane has recently been proposed, involving non-orthogonal orbitals[67], which shows that it is possible for a type of hybridisation to exist, in which the angle between the orbitals remains 60°. Thus the question of the special nature of the bonds in cyclopropane cannot be considered as settled.

What has been said above applied, in the main, to the simplest heterocyclic compounds. A particular feature here is that the strain in a heterocyclic compound containing oxygen or sulphur in the ring is always less than the strain in a cycloalkane with the same ring size. This is well illustrated by the thiacyclanes, for which there are fairly complete data on heats of combustion[68,69,70] (Table 3). The smaller strain in thiacyclanes is explained by the fact that the divalent sulphur atom is devoid of substituents, so that the number of interactions between non-bonded atoms is less[34]. The decrease in the conformational strain when a CH_2 group in a ring is replaced by a divalent hetero-atom can also explain the fact that the four-membered ring, trimethylene sulphide, is apparently flat[71] (C_{2v} symmetry). A five-membered ring is still non-planar in the case of the thiacyclanes, but in contrast to cyclopentane, "pseudo--rotation" is difficult in thiophane (i.e. movement of the position of greatest deviation from the plane, among the atoms)[72].

The heats of combustion of the simplest oxygen heterocycles are given in Table 4 and do not require special explanation. Unfortunately, no calorimetric figures are available for trimethylene oxide but, as far as one can judge from micro-wave[75] and vibrational spectra[76], the four-membered oxygen-containing ring has a flat structure like its sulphur analogue.

TABLE 3. Heats of combustion of thiacyclanes.

No. of atoms in ring n	Heat of combustion $-\Delta H_c$ (g), kcal mole^{-1}		Strain, kcal mole^{-1}	
	cyclanes (see Table 1)	thiacyclanes[68]	cyclanes (see Table 1)	thiacyclanes (see Note)
3	499.8	344.4	27.6	19.6
4	655.8	502.0	26.0	19.8
5	793.6	643.0	6.5	3.4
6	944.6	797.0	0	0
7	1108.3	958 5	6.3	3.9

Note. The values of the heats of combustion of the thiacyclanes are given for combustion to CO_2 (g), H_2O (l), and S (rhombic). The strain of the thiacyclanes, relative to thiacyclohexane, the strain of which is assumed to be zero, can be expressed as the difference between the observed heat of combustion and that calculated for the same, hypothetical, unstrained ring:

$$-\Delta H_{c,\text{excess}} = -\Delta H_{c_n} + \Delta H_{c_6} + (n-6)\,\Delta H_{c_{CH_2}},$$

where $\Delta H_{c,\text{excess}}$ is the strain, ΔH_{c_n} is the heat of combustion of an n-membered ring compound, ΔH_{c_6} the heat of combustion of a 6-membered ring compound and $\Delta H_{c_{CH_2}}$ the normal increment for CH_2 in cyclohexane and n-alkanes, equal to 157.4 kcal/mole (for the calculation of strain, see Skuratov et al.[73]).

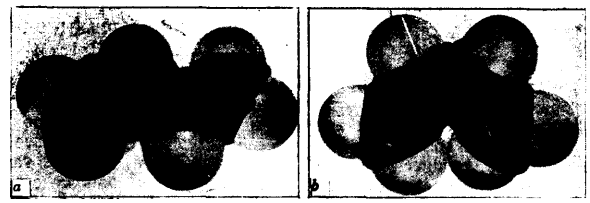


Fig. 3. Conformations of a butadiene molecule: *a*) transoid; *b*) cisoid.

TABLE 4. Heats of combustion of oxacyclanes.

No. of atoms in ring n	Heat of combustion $-\Delta H_c$ (g), kcal mole^{-1}	Strain, kcal mole^{-1}	Reference
3	312.6	26.2	74
5	605.8	4.6	73
6	758.6	0	73

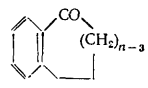
As far as the heats of combustion of the saturated nitrogen heterocycles are concerned, that of ethyleneimine is the only one that has been determined recently*[77]. Apart from this, there are some old data for piperidine[78]. If one reckons piperidine to be unstrained and takes $-\Delta H_c$ (g) for ethyleneimine and piperidine as 384.9 and 834.1 kcal/mole respectively, one can estimate the strain in ethyleneimine to be about 23 kcal/mole, a figure that is little different from those for other three-membered rings (Tables 3 and 4). Conformational strain in cyclic compounds possessing a conjugated system of double bonds takes an unusual form. It is well known that the preferred conformation of a conjugated system is a coplanar one in which the single bonds are transoid to each other. For example, Fig. 3*a* depicts such a conformation for butadiene. A *cis*-conformation for conjugated dienes is less favourable, as is clearly shown by their ultra-violet spectra (the intensity of the absorption maxima of *cis*-dienes is about half that of *trans*-dienes).

In cyclic compounds, coplanarity of the diene system is possible in only a few cases. Non-coplanarity results in an increased energy content and in partial or, with large interplanar angles, complete disappearance of the properties of a conjugated system. This variety of conformational strain is known as "steric hindrance of the delocalisation of valency electrons"[28] or "steric hindrance of mesomerism"[79]. It

* After this paper had been despatched for printing, some data on the heats of combustion of pyrrolidine have been published[189]: $-\Delta H_c$ (l) = 673.80 ± 0.1 kcal/mole; ΔH_{vap} = 8.98 ± 0.015 kcal/mole and consequently $-\Delta H_c$ (g) = 682.8 ± 0.1 kcal/mole, which agrees well with the existing data for 3- and 6-membered saturated nitrogen-containing rings.

can easily be detected with the help of ultra-violet absorption spectra, and also manifests itself in a number of chemical properties. For example, the absorption coefficient of the *cis*–*cis*-cycloalka-1,3-dienes decreases progressively from cyclohexadiene to cyclooctadiene[80]. In the case of *cis*–*cis*-cyclodeca-1,3-diene,[81] conjugation of the double bonds is not manifested at all — the ultra-violet spectrum does not contain a maximum in the 215–230 mμ region, characteristic of conjugated dienes. It is interesting to note that *cis*–*cis*-cyclodeca-1,3-diene[81] and *cis*–*cis*-cycloocta-1,3-diene[82] do not form adducts with maleic anhydride.

A similar effect is observed in a number of 1,2-benzocycl-1-ene-3-ones[83,84], 1,2-benzolactams[85] and other similar condensed compounds[79]. Thus, for the 1,2-benzocycl-1-ene-3-ones there is a decrease in the intensity of the



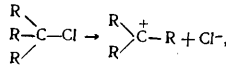
absorption maximum at 240–250 mμ, characteristic of aliphatic-aromatic ketones, as the ring size increases from 5- to 10-membered. This is explained by the increasing deviation of the plane of the carbonyl group from the plane of the benzene ring, as the ring size increases.

2. TYPES OF STRAIN. THE EFFECT OF STRAIN ON THE REACTIVITY OF CYCLIC COMPOUNDS

It has been known for a long time that ring-strain materially affects the reactivity of organic compounds. For instance, three- and four-membered ring compounds, in contrast to their higher cyclic homologues, readily take part in reactions accompanied by ring fission. This is understandable, since such reactions are accompanied by the evolution of heat (e.g. the free energy of isomerisation of cyclopropane and cyclobutane to olefins is -9.99 and -11.73 kcal/mole respectively[59], while that of cyclopentane is +5.04 kcal/mole[59]).

There are, however, much finer distinctions between the reactivities of cyclic compounds, which are found in substitution reactions and do not involve ring fission. For example, nucleophilic substitution reactions are very difficult in three-, four- and six-membered rings, and considerably easier in five- and seven-membered rings. At first glance, these differences are quite inexplicable. Neither a polar effect nor a steric effect, in its usual sense ("steric hindrance"), can explain peculiarities of this sort in the reactivity of cyclic compounds.

Some interesting and unusual ideas have been developed recently by Brown[86,87], who considers that steric factors can assist a reaction (steric assistance) as well as hinder it*. This viewpoint is reflected in his interpretation of the results of studies of cyclic systems (see below); it may be illustrated here by some data obtained by Brown and Fletcher[88] in an investigation of the effect of structure on the ease of hydrolysis of tertiary aliphatic halides. According to Brown and Fletcher this reaction, which proceeds by the



carbonium-ion mechanism, is facilitated by the decrease in strain occurring when the original strained molecule is converted to a flat, unstrained ion. It is well known that the ready hydrolysis of tertiary halides can be explained either by the total inductive effect of the three alkyl groups, which facilitates ionisation, or by stabilisation of the carbonium ion due to hyperconjugation. However, examination of the two series $(CH_3)_{3-x}(C_2H_5)_xCCl$ and $(CH_3)_{3-x}(\text{iso-}C_3H_7)_xCCl$ does not reveal the regular behaviour that would be expected on the above considerations. While, in the first series, an increase in the hydrolysis rate occurs each time an ethyl group is introduced, in the second series, exchange of one CH_3 group by an isopropyl group leads to a decrease of hydrolysis rate, while the second and third exchanges result in an increase. Whatever the nature of the effect evoked by the first isopropyl group it should have been maintained when the second and third groups were introduced. In the opinion of Brown and Fletcher[88] a steric effect is the only simple explanation of the influence on hydrolysis rate of the accumulation of isopropyl groups. Two such groups result in a crowding at the reaction centre, which facilitates ionisation.

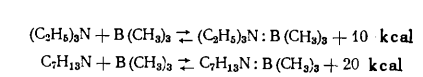
On the basis of a great deal of experimental material, relating mainly to acyclic compounds, Brown originally introduced the idea of two types (*F* and *B*) of steric strain that became evident in a study of chemical reactivity. One of these, the so-called *F*-strain, "is an enhancement of steric strain, due to the spatial interference between groups attached to two atoms, which arises during the formation of a bond between these atoms".[86] It is usually detected in cases where the product of interaction of two molecules contains bulky substituents in the vicinity of the atoms, forming the bond between the molecules.

This may be illustrated by examples from Brown's work[86]. The basic strength of the pyridine bases increases in the order

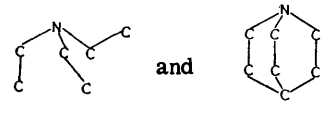
pyridine < 2-picoline < 2,6-lutidine

due, in the author's view, to the inductive effect of the methyl groups. This order of basicity is found in a study of the heats of reaction with a proton acid (methanesulphonic acid). However, with Lewis acids, e.g. boron trifluoride, which naturally have a larger volume than a proton, the ability to form salts increases in the reverse order. This can be explained by the repulsive forces acting between the nuclear substituents and the fluorine atoms. It is interesting that the particularly bulky trimethylboron does not react with 2,6-lutidine, or with 2-t-butylpyridine.

As a second example, triethylamine and quinuclidine may be cited. The basic strengths of these (towards a proton) are about the same, but their molecular compounds with trimethylboron differ markedly in stability:



i.e. the second is the more stable. The difference is due to the different spatial relationships of the substituents in the two bases:



i.e. in the first, the three ethyl groups are free to rotate about the C–N bonds, so that by their interaction with the

* It should be noted that such an idea is not new and was previously developed using hexaphenylethane derivatives as examples.

methyl groups of the trimethylboron, repulsive forces can be set up. In the second base, the substituents on the nitrogen atom are held fixed so that this sort of steric interaction is impossible.

Thus *F*-strain manifests itself as a force which hinders the formation of an addition compound or tends to separate the two parts of an existing adduct. It does not act within a molecule but in the plane between two components of a molecule ("in front") and was called *F*-strain for this reason. A characteristic of this type of strain is its dependence on the volume of both components.

Brown contrasted the concept of *F*-strain with that of *B*-strain, in connection, however, with acyclic systems. It is useful, nevertheless, to understand these concepts since they are related to other of Brown's views, discussed below. An example, quoted by Brown and his coworkers [89] will be considered. It is well known that the methylamines form a series in order of basic strength:

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3.$$

The stabilities of their trimethylboron addition compounds, characterised by the dissociation pressures, are in the same order. The authors conclude that the affinity of these bases for $B(CH_3)_3$ is, on the whole, the same as their affinity for a proton, i.e. that their relative basic strengths do not depend on the nature of the acid component and hence on its steric features. Thus the degree of stability of these addition compounds must be related to the steric relationship of the groups attached to the nitrogen atom. The angle between the bonds of tetravalent nitrogen is equal to the tetrahedral angle, whereas in amines it is somewhat greater. According to Brown, the change to the ionic state here involves a diminution of the angle. This is the cause of the strain, called by the authors "*B*-strain"*. It is localised behind (hence *B*) the reactive centre, in this case the nitrogen atom and, as already stated, does not depend on the steric nature of the second component. Essentially, *B*-strain is brought about by deformation of valency angles and interaction of non-bonded atoms, i.e. by the causes responsible for the whole phenomenon of strain.

In a study of the reactivity of cyclic compounds, Brown introduced the concept of so-called *I*-strain (from "internal") [93,94]. This enables on to explain many features of the chemical behaviour of cyclic compounds and to classify much varied material.

In order to clarify what Brown meant by "*I*-strain", we shall quote some data obtained in an examination [93] of the properties of addition compounds of trimethylboron with several organic bases, and the authors' interpretation. Table 5 shows the extent of thermal dissociation of these compounds, which is a measure of their stability. The authors consider that the lower stability of the diethylamine

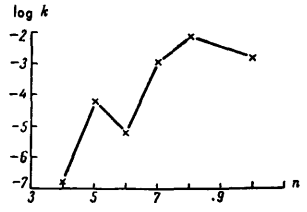


Fig. 4. Relation between the decomposition rate of azodinitriles and ring size (*n*).

TABLE 5. Thermal dissociation of trimethylboron complexes of amines.

Base	ΔH_{diss}	K_{diss} at 100°
Dimethylamine	19.26	0.0214
Diethylamine	16.31	1.22
Ethyleneimine	17.59	0.0284
Trimethyleneimine	22.48	0.000322
Pyrrolidine	20.43	0.00350
Piperidine	19.65	0.0210

complex compared to the trimethylamine complex can be ascribed to the greater volume of the ethyl groups. The increase of stability on passing to the piperidine complex, manifested by a fall in the rate constant and a rise in the heat of dissociation, is related to the fact that the methylene groups in a piperidine molecule are not free to rotate and cannot interact with the methyl groups of trimethylboron. Comparision of the data for the piperidine and pyrrolidine complexes shows that the second is the more stable. Since in aqueous solution piperidine and pyrrolidine have equal basic strengths, one may conclude that *F*-strain is present in these two compounds as well. In pyrrolidine its magnitude is less, because the two α-CH_2 groups are "pulled away" from the $B(CH_3)_3$ molecule to a greater extent than in piperidine — in other words, because of the smaller steric effect of two CH_2 groups in pyrrolidine. The trimethyleneimine complex with trimethylboron is even more stable, a fact that can again be explained by the geometry of the ring. However, with ethyleneimine-trimethylboron there is an unexpected decrease of stability. This points to the operation, in the three-membered ring, of another effect which becomes more important than the *F*-strain. The relative stabilities of the cyclic complexes mentioned may be expressed as the series $6 < 6 < 4 \gg 3$. The heat of dissociation of trimethyleneimine-trimethylboron is some 5 kcal greater than that of ethyleneimine-trimethylboron. *F*-strain should be less in ethyleneimine. Consequently, the 5 kcal must be ascribed to some other form of destabilisation. The authors of the work quoted consider that this is caused by the so-called internal strain of the ring, brought about by the change in the valency angle when the free cyclic imine is converted to a compound containing a tetravalent

* There are comparatively few data, in the literature, concerning the magnitude of the valency angle of nitrogen in amines, and these are insufficiently accurate and frequently contradictory. For example, two values are quoted [90] for the CNC angle in dimethylamine: 108° ± 4° and 111° ± 3°. It may be said that in the case of the methylamines, the observed deviation from the tetrahedral angle is within the experimental error. There are therefore good grounds for the view that β-strain is negligible in the methylamines and that the anomalies referred to cannot be ascribed to its influence [91,92]. At the same time, in highly branched tertiary amines, *B*-strain may exert an appreciable influence on reactivity; however, this has not yet been confirmed experimentally.

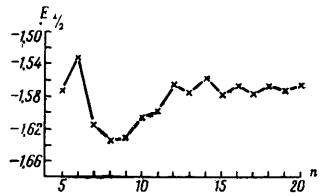
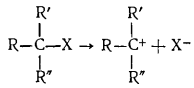


Fig. 5. Dependence on ring size (n) of the half-wave potential ($E_{1/2}$) for the polarographic reduction of the products of reaction between cyclic ketones and Girard's reagent T.

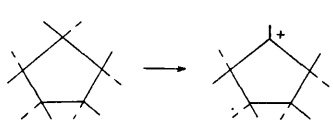
nitrogen atom. For such an atom, the tetrahedral disposition of valencies will be the most stable. Thus the strain in ethyleneimine-trimethylboron is measured by 109°28'–60°, exceeding the strain in free ethyleneimine, which, from a quantum-mechanical picture of a nitrogen atom, was estimated to be 90°–60°. All that has been said throws some light on the following definition:

"I-strain is the increase of internal strain of a cyclic structure, brought about by the disturbance of valency angles and conformations that accompany a change in the coordination number of an atom in the ring during reaction"[86].

Several examples from the carbocyclic field will serve as further examples. The monomolecular reaction of nucleophilic substitution (S_N1) proceeds via the formation of a carbonium ion:



There is thus a change in the coordination number of carbon from 4 to 3. What effect does this have on the strain of a cyclic compound, if the carbon atom affected forms part of a ring? An atom with a coordination number of 4 is tetrahedral with an optimal valency angle of 109°28'; for a coordination number of 3, planar symmetry with a valency angle of 120° is the most favourable. In small rings (three- and four-membered), where Baeyer strain plays an important part, such a change of valency angle must lead to increased strain. In fact, with the optimal angle of 109°28', the change of valency angle in a three-membered ring is 109°28'–60° = 49°28'; with an angle of 120°, this change is greater, viz. 120°–60° = 60°. In 5-, 7-membered, and intermediate rings, the chief source of strain is interaction between non-bonded atoms. For example, the idealised planar structure of cyclopentane contains 5 unfavourable eclipsed conformations, or, in Brown's terminology, there are in such a ring 10 interactions brought about by C–H bond oppositions; this gives rise to the strain in a five-membered ring. When one hydrogen atom is removed, the number of C–H bonds is 9, while the "number of interactions" between neighbouring, mutually eclipsed hydrogen atoms, is 6. As a result there is a considerable decrease of conformational strain.

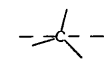


Brown's opinion concerning a six-membered ring is that a change of coordination number from 4 to 3 is in this case unfavourable as it leads to a less symmetrical system, in which "bonds of positions" make their appearance.

The reverse process, i.e. increase of coordination number from 3 to 4, e.g. by addition to a C=O group, is facilitated in six-membered and small rings since it is associated with a decrease of strain, while in 5-membered, 7-membered, and intermediate-sized rings it is less favourable.

It is natural to suppose that, if the change of coordination number occurs at the rate-determining stage of a reaction the associated change of internal strain of the ring will affect the reaction kinetics. There are, in fact, many examples in which the ratio of reaction rates for different rings is in good agreement with predictions of the I-strain theory. This applies not only to addition to carbonyl groups and S_N1 reactions but also to radical reactions and S_N2 reactions.

In the case of radical reactions, the above discussion of S_N1 reactions also applies. In S_N2 reactions, the transition complex has a coordination number of 5. For small rings, the effect of changing the coordination number from 4 to 5 is the same as changing it from 4 to 3, since the three groups not participating in the substitution process are arranged



in one plane with a central atom, while the valency angle is 120°. For rings in which conformational strain is predominant, this picture may be somewhat distorted owing to interaction of the fifth ligand with non-bonded atoms, i.e. the acceleration of a reaction, in comparison with a six-membered ring, is appreciably less than in an S_N1 reaction.

TABLE 6.

Type of reaction	Rings						
	small		normal		intermediate		large
	3-	4-	5-	6-	7-	8- to 12-	13- and larger
S_N1, S_N2, and free radical	very slow	slow	fast	slow	fast	fast	medium rate
Addition to carbonyl group	very fast	fast	slow	fast	slow	slow	medium rate

Thus, the size of the ring can affect reaction rate in different ways, depending on the type of reaction[86] (Table 6).

A number of examples illustrating the effect of I-strain on reaction rate will now be considered. It has been known for some time that many nucleophilic substitution reactions proceed slowly with cyclopropyl, cyclobutyl, and cyclohexyl derivatives and considerably faster with derivatives of other rings. Thus Gustavson[95] in 1891 found that chlorocyclopropane reacted with great difficulty with alcoholic caustic potash; according to his estimate, the reactivity of chlorocyclopropane in this reaction was even lower than that of 1-chloroprop-1-ene, which contains a vinyl chlorine atom. At about the same time, Perkin[96] drew attention to

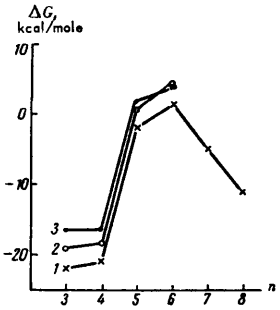


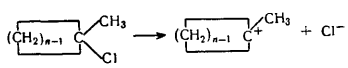
Fig. 6. Semi-empirical values of the free-energy change for the hypothetical polymerisation of cycloalkanes: 1) unsubstituted cyclanes; 2) methyl-substituted cyclanes; 3) 1, 1-dimethyl--substituted cyclanes.

the low rate of reaction between chlorocyclobutane and potassium iodide. Chlorocyclohexane also exhibits an anomalously low reactivity towards potassium iodide[97]; the rate constant of this reaction is more than 150 times smaller than in the case of isopropylchloride, chosen as an example of a secondary aliphatic chloride. Cyclohexyl halides react appreciably more slowly with pyridine and piperidine than do secondary aliphatic halides[98]. A comparison of the reactivity of cyclopentyl, cyclohexyl, and cycloheptyl bromides with various bases[99] showed that cyclohexyl bromide was the least reactive in these reactions and cyclopentyl bromide the most reactive.

The kinetics of S_N1 reactions of various rings have been studied in detail for the solvolysis (with acetic acid) of 1-chloro-1-methylcycloalkanes (Table 7) and cycloalkyl-*p*--toluenesulphonates (Table 8).

The kinetics of S_N2 reactions have been studied in comparatively few cases. In the literature, there are data for the reaction of cyclic bromides with potassium iodide in acetone[101,104,105] and the exchange of iodine in cyclic iodides, using labelled iodine[106] (Tables 9 and 10)*.

TABLE 7.



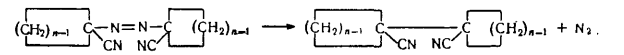
(from data of Brown and Borkowski[100]).

n	k_1, h^{-1}, at 25 °C	Relative rate
4	0.00224	0.211
5	1.32	124
6	0.0106	1.00
7	1.15	108
8	3.03	286
9	0.465	43.9
10	0.188	17.7
11	0.127	12.0
13	0.0302	2.85
15	0.0192	1.81
17	0.0201	1.90
$(CH_3)_3$ CCl	0.0302	2.85

* After this paper had been despatched for printing, some new work appeared[190] which substantially supplemented the existing data on the kinetics of S_N2 reactions for cyclic compounds and confirmed the earlier conclusions about the reactivity of compounds with rings of different size in this type of reaction.

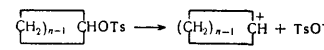
Radical reactions of cyclic compounds, involving a change in the coordination number of an atom in the ring, have been comparatively little studied. However, such data as exist are apparently not inconsistent with the *I*-strain concept. Thus an investigation of the kinetics of hydrogen removal by a methyl radical from cycloalkane molecules[107,108] showed that reactivity varied with the size of the ring, in the order $C_5 > C_6 > C_4 \gg C_3$.

Some very interesting results were obtained by Overberger and coworkers from a study of the kinetics of the decomposition of azodinitriles, containing cyclic groups[109]:



It had been shown earlier that this radical reaction was

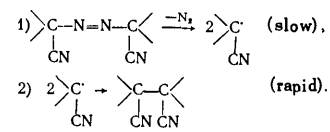
TABLE 8.



n	Relative rate at 70°C	Reference
3	$2 \cdot 10^{-5}$ (at 60°C)	101
4	11.3	102
5	14.0	102
6	1.00*	102
7	25.3	102
8	191	102
9	172	102
10	380	103
11	48.9	102
12	3.25	102
13	3.50	102
14	1.32	102
15	2.19	102
17	2.17	102
20	1.80	103

* $k_1 = 2.37 \cdot 10^{-5}$ sec^{-1}; for $(n\text{-}C_3H_7)_2$ CHOTs the relative rate was found to be 1.33.

of first order:



It is easy to see that the slow step, which determines the reaction rate, involves a change in the coordination number of the carbon atom from 4 to 3. It is not surprising that the rate of this reaction depends substantially on the size of the ring. The results obtained[109] are in good agreement with the concept of *I*-strain (see Table 11 and the curve in Fig. 4).

It is particularly important that the rate of decomposition of the azodinitriles does not depend on the solvent[111], so that a solvent effect, which can affect reaction rate to such a great extent, is in this case absent. According to Overberger[109], the rate of decomposition of azodinitriles

TABLE 9.

$$(CH_2)_{n-1}CHBr + I^- \rightleftharpoons (CH_2)_{n-1}CHI + Br^-$$

n	$k_2 \times 10^5$, litres mole^{-1} sec^{-1}, at 25°C	Reference
3	no reaction even at 100°	101
4	0.00980	104
5	2.08	104
6	0.0129	104
7	1.27	104
8	0.69	105

is an accurate measure of the differences in the strain of rings.

Reactions involving addition to a carbonyl group proceed at noticeably different rates for rings of different size. For example, the formation of phenylhydrazones[112], oximes[113], and semicarbazones[114], which can be represented as additions to a carbonyl group followed by elimination of water,

$$R_2C{=}O + H_2N{-}X \rightleftarrows R_2C\begin{matrix}O^-\\ \diagup\\ \diagdown\\ {}^+NH_2{-}X\end{matrix} \xrightarrow{-H_2O} R_2C{=}N{-}X,$$

and the formation of bisulphite derivatives[113], proceed fastest with cyclohexanone, slower with cyclopentanone, and slower still with cycloheptanone. The same order of reactivity, i.e. $C_6 > C_5 > C_7$, is found in the reaction of perbenzoic acid with cycloalkanones[115] (Table 12).

This reaction proceeds according to the scheme:

$$1)\ >C{=}O + C_6H_5COOOH \rightarrow >C\begin{matrix}OH\\ \diagup\\ \diagdown\\ OOCOC_6H_5\end{matrix} \quad \text{(slow)},$$

$$2)\ >C\begin{matrix}OH\\ \diagup\\ \diagdown\\ OOCOC_6H_5\end{matrix} \rightarrow >C\begin{matrix}OH\\ \diagup\\ \diagdown\\ O^-\end{matrix} + C_6H_5COO^- \quad \text{(rapid)},$$

$$3)\ >C\begin{matrix}OH\\ \diagup\\ \diagdown\\ O^-\end{matrix} \rightarrow >C{=}O + H^+ \quad \text{(rapid)}.$$

Thus, additions to a carbonyl group also proceed fastest with cyclohexanone.

Naturally, for the reverse reaction (dissociation to form a carbonyl group) the order is reversed. For example, the dissociation constants of the hemiketals of cyclic ketones[116] clearly indicate that the hemiketals of cyclobutanone and cyclohexanone are much more stable than those of other cyclic ketones or of aliphatic ketones (Table 13).

We may note that the dissociation constant of the hemiketal of di-n-propyl ketone was found by Wheeler[116] to be 89.0. Also, cyclopropanone is quite unknown in the free state and exists only as the hydrate and the hemiketal. Attempts to prepare the semicarbazone lead to rupture of the three-membered ring[117].

The addition of hydrogen (hydrogenation with sodium borohydride[118], see Table 14) and hydrogen cyanide (for dissociation constants of cyanhydrins[119], see Table 15) to carbonyl groups have been studied in great detail.

The latter data are particularly interesting since they refer to an equilibrium and hence characterise the relative stabilities of the components. The Table shows that with intermediate rings, the keto-form is the most stable; this conforms to the ideas of *I*-strain.

Results consistent with the idea of *I*-strain were also obtained by the polarographic reduction of the products of the reaction between Girard's reagent T and cyclic ketones[120] (Fig. 5). The mechanism of this reaction may be represented as follows:

$$1)\ >C{=}NNHCOCH_2\overset{+}{N}(CH_3)_3 + H^+ + e^- \underset{\text{reversible}}{\rightleftarrows} >\dot{C}{-}NHNHCOCH_2\overset{+}{N}(CH_3)_3,$$

$$2)\ >\dot{C}{-}NHNHCOCH_2\overset{+}{N}(CH_3)_3 + H^+ + e^- \xrightarrow[\text{irreversible}]{} >CHNHNHCOCH_2\overset{+}{N}(CH_3)_3.$$

In this case, the half-wave potential (i.e. the energy used for reduction and hence for changing the coordination number of carbon from 3 to 4) is least for a six-membered ring and greatest for intermediate-sized rings.

I-strain is only one of the factors that determine relative reaction rates of cyclic compounds. Remarking on this, Brown[100] pointed out that such factors as *F*-strain, solvation, the influence of neighbouring groups, etc., can play an important and sometimes predominant part. Accurate accounting for all these factors is extremely difficult, so that it is not surprising that the nature of the relation between reactivity and ring size is different for different reactions and different types of cyclic compound. For instance, the rate of solvolysis of 1-chloro-1-methylcyclobutane in acetic acid[100] is considerably less than the rate of solvolysis of the five-membered 1-chloro-1-methylcyclopentane and less than that of the six-membered ring; at the same time, for solvolysis of chlorocycloalkanes in 50% ethanol[101], the reaction rate for the four-membered ring is three times as fast as that for the five-membered ring and forty times as fast as that for the six-membered ring.

TABLE 10.

$$(CH_2)_{n-1}CHI + I^{*-} \rightleftarrows (CH_2)_{n-1}\dot{C}HI + I^-$$

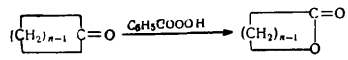
(from data by Van Stratenetol.[106])

n	5	6	7	8	15
k_2, litres mole^{-1} sec^{-1} at 25°C	0.88	0.0084	1.2	0.28	0.099

TABLE 11. Kinetics of decomposition of azodinitriles[109].

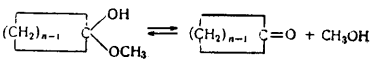
n	$k_1 \times 10^4$, sec^{-1}, at 80°C	$\Delta E_{act.}$, kcal mole^{-1}
4	0.00173	32.1±1.0
5	0.726	33.8±0.9
6	0.063	35.4±0.6
7	12.22	27.5±0.9
8	83.5	25.9±0.9
10	18.42	28.0±0.7

TABLE 12.



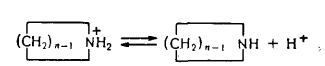
n	5	6	7
$k_2 \times 10^3$, litres mole^{-1} sec^{-1}, at 27°C	17.3	106	1.69

TABLE 13.



n	4	5	6	7	8
k_{diss} at 25°C	1.11	15.1	2.16	53.5	268

The relation between the basicities of the cyclic imines, determined by the equilibrium constant of the reaction*



can be explained fairly easily on the basis of *I*-strain, for $6 \leqslant n \leqslant 20$.[121] Piperidine is the most basic in this series; this corresponds to the greater stability of a tetrahedral nitrogen atom in a six-membered ring, compared to one in other rings. The intermediate-sized rings are the least basic, i.e. nitrogen with a coordination number of 3 is here relatively more stable. At the same time, examination of the basic strengths of the cyclic imines having $3 \leqslant n \leqslant 6$ [122] shows that they are similar for $n = 4, 5, 6$ while for ethyleneimine K_b is anomalously low (Table 16).

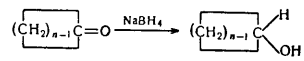
Brown attempted to explain the different basic strengths of the imines (in their reaction with trimethylboron, see Table 5) [95] by the competing influences of *I*- and *F*-strain. Searles et al.[122] consider that these differences are determined by the nature of the electron-density distribution in the cyclic-imine molecules. In this case, it would appear that both steric and polar factors play an important part. The importance of steric factors is evident, if only from the fact that the relation between ring size and basic strength determined by the dissociation constants of the trimethylboron complexes, differs from that for proton-addition.

In some cases, the influence of polar factors can be taken into account. For example, the data on the rates of alkaline hydrolysis of lactones[123,124] (Table 17) clearly fall into two groups. Lactones with a ring-size of up to 8 members hydrolyse relatively quickly. Those with 10–16-membered rings hydrolyse at rates some hundred of times slower. This phenomenon was explained by the fact that the ester group has different conformation, depending on the ring size[79,124]. In rings of the usual size, the energetically more favourable planar transoid conformation, inherent in esters, cannot exist since it would involve considerable



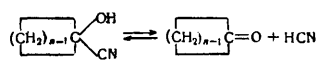
deformation of the valence angles. The cisoid ester conformation has an excess of free energy of about 3.6 kcal/mole over the transoid. The greater reactivity of lactones with usual-size rings compared to aliphatic esters is thus understandable. In lactones with intermediate-sized and large rings, the transoid ester conformation can exist. Their hydrolysis rates are closely similar to those of acyclic esters. A comparison of the dipole moments and boiling points of lactones shows that the change from a cisoid to a transoid conformation occurs between an eight- and nine-membered ring. An eight-membered lactone is mainly in the *cis*-form with a small amount of the *trans*-form present, while with a nine-membered lactone, the *trans*-form predominates. We may note that the relation between rate of

TABLE 14.



n	$k_2 \times 10^4$ litres mole^{-1} sec^{-1}, at 0°C	ΔE_{act}, kcal mole^{-1}
4	264	8.6
5	7.01	9.8
6	161	5.8
7	1.02	10.2
8	0.0781	11.9
9	0.0316	12.2
10	0.0132	13.1
11	0.0235	12.0
12	0.182	11.3
13	0.194	11.8
15	0.420	11.5
17	0.593	10.7
di-n-hexyl ketone	0.454	11.5

TABLE 15



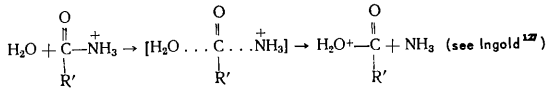
n	$K_{diss} \times 10^2$ at 22°-23°C	ΔG, kcal mole^{-1}
5	2.1	−2.4
6	0.1	−4.2
7	13	−1.3
8	86	−0.1
9	170	+0.3
10*		
11	112	+0.1
12	31	−0.7
13	26	−0.8
14	6	−1.7
15	11	−1.4
16	9	−1.5
17	12	−1.3
18	10	−1.4
19	10	−1.4
20	7	−1.6
di-n-octyl ketone	7	−1.6

* The constant for this reaction characterises the acid dissociation constant of the corresponding cation, i.e. it is smaller the more basic the amine. The constants in Table 16 appear to be true basic dissociation constants, i.e. they correspond to the reaction $RNH + H_2O \rightleftharpoons RNH_2^+ + OH$ (Ed. of Translation).

* K_{diss} for the cyanhydrin of cyclohexanone is very large. Its value could not be accurately determined because the equilibrium mixture contains practically no cyanhydrin.

hydrolysis and ring size for cisoid lactones confirms the idea of *I*-strain (a maximum for six-membered and small rings).

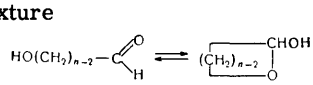
The rates of alkaline hydrolysis of five-, six-, and seven--membered lactams bear the following relation to ring size[125]: $6 > 5 > 7$. This can be explained from the point of view of *I*-strain, in a similar way to the alkaline hydrolysis of lactones. Similar results were obtained from a study of the kinetics of acid hydrolysis of lactams with rings of from 5 to 8 members. The rates of hydrolysis for the eight-, five-, seven-, and six-membered lactams were in the ratio 1.1 : : 2.1 : 4.75 : 17.5 respectively. If the acid hydrolysis of amides proceeds via proton addition to the nitrogen atom (rapid stage), while the slow, rate-determining step involves the formation of a complex in which the carbonyl carbon has a coordination number of 4



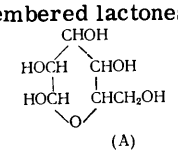
it is possible to explain the observed relative reaction rates from the point of view of *I*-strain.

The conception of *I*-strain arose following the analysis of a large quantity of material concerning the reactivity of various cyclic systems. Naturally, the most detailed data available were those for five- and six-membered rings. Consideration of these data led Brown to a further generalisation[128] concerning the relative stability of five- and six--membered rings. "An exocyclic double bond in a five--membered ring is less reactive and more stable than a corresponding exocyclic double bond in a six-membered ring. Reactions which involve the formation or retention of an exocyclic double bond in a five-membered cyclic derivative will be facilitated relative to the corresponding reactions which involve formation or retention of an exocyclic double bond in a six-membered cyclic derivative. Reactions which involve loss of an exocyclic double bond will be more favoured in a six-membered ring compound than in the corresponding five-membered ring compound"[129]. This conclusion is evidently supported by the data quoted above, concerning the reactivity of cyclic ketones in reactions involving the keto group.

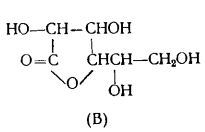
It is interesting to compare the data concerning ring--fission in five- and six-membered heterocycles containing an exocyclic double bond and in saturated compounds. It has already been noted that five-membered lactones are more stable to hydrolysis than six-membered ones. However, the internal cyclic hemiacetals of ω-hydroxyaldehydes which contain a six-membered ring are more stable than those which contain a five-membered ring[130]. The equilibrium mixture



contains 11.4% free aldehyde when $n = 5$ and 6.1% when $n = 6$. Thus, in the absence of an exocyclic double bond a six--membered ring is more stable, otherwise, a five-membered ring. Brown thus explains the fact that sugars (hydroxyaldehydes) prefer to form six-membered pyranose (A) rings, while the saccharic acids (hydroxyacids) prefer five-membered lactones (B):



(A)



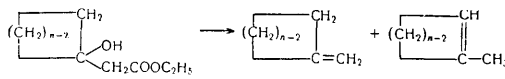
(B)

TABLE 16. Basic dissociation constants of cyclic imines.

n	$K_b \times 10^4$, at 25°C
3	0.011
4	20
5	18
6	16.6

It must not be concluded that five-membered ring compounds with an exocyclic double bond are generally more stable than their isomers with an endocyclic double bond, or that for six-membered rings, the *exo*-form is always less stable than the *endo*-form*.

It should be pointed out that, even in its strictest sense, Brown's generalisation does not always prove to be correct. Thus, the mixture of olefins, obtained by heating the esters of cycloalkanolacetic acids[133]:

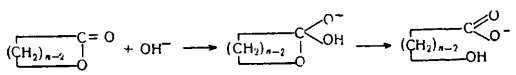


contains less of the *exo*-isomer with a five-membered ring than with a six-membered ring, not more, as should be the case according to Brown (39% for $n = 5$ and 62% for $n = 6$). The ease of isomerisation of the exocyclic isomer to the endocyclic isomer is about the same in both cases.

A study of the heat of hydrogenation of exo- and endocyclic olefins[134] (Table 18), showed that the *exo*-form is relatively less destabilised with a six-membered ring than with a five-membered ring. As Table 18 shows, the difference between the heats of hydrogenation of *exo*- and *endo*-isomers, brought about by the greater energy content of the *exo*-form (or, its lower stability), is greater for

* Similar incorrect interpretations of Brown's views have been repeatedly met with in the literature (see, for example, Fleck[131]). This can largely be attributed to lack of clarity in their formulation and to an insufficiently critical selection of material in the paper by Brown and collaborators[128], which generalised the properties of 5- and 6-membered rings. In the principal works devoted to *I*-strain, Brown links kinetic data inseparably to reaction mechanism, which enabled him to create an extremely orderly system of ideas. On the other hand, in the paper referred to[128], a large number of facts are presented, relating to various classes of compounds and concerning the relative stability of 5- and 6-membered rings, without a detailed discussion of the corresponding reaction mechanism. It is not surprising that such a one-sided approach should occasionally lead to contradictions. For example, Brown[128] points to the tendency of δ-valerolactone to polymerise and to the absence of a similar tendency in γ-butyrolactone as facts confirming the relatively greater stability of five-membered rings with an exocyclic double bond compared to six-membered ones. It would seem that a similar relationship should exist for the lactams. In fact, however, α-pyrrolidone polymerises much easier than α-piperidone[132]. Polymerisation processes are extremely complex and, without a thorough study of their mechanism, it is not permissible to make any broad generalisations about different classes of chemical compounds.

TABLE 17.



(hydrolysis by NaOH in water-dioxane medium according to data of Huisgen and Ott[124]).

n	$k_2 \times 10^4$, litres mole^{-1} sec^{-1}, at 0°C	Dipole moment in benzene D	$B.p.$ at 10–11 mm Hg, °C
4	350 000 (at 20°C) [123]	3.8	51
5	1 480	4.09	79–80
6	55000	4.22	97–98
7	2 550	4.45	104–106
8	3 530	3.70	80–82
9	116	2.25	72–73
10	0.22	2.01	86–87
11	0.55	1.88	100
12	3.3	1.86	116
13	6.0	1.86	130
14	3.0	1.86	143
16	6.5	1.86	169
n-butyl ester of caproic acid	8.4	1.79	83°

TABLE 18. Heats of hydrogenation of *exo*- and *endo*-isomers.

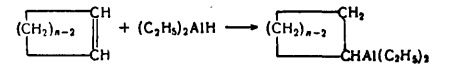
Olefin	*exo*-	$CH_2=$	CH_3-	$CH_3CH=$	$CH_3CH=$
	endo-	$CH_2=$	CH_3-	CH_3CH_2-	CH_3CH_2-
$\Delta H_{hydrog.}$, kcal mole^{-1}, at 25°C		−26.9	−27.8	−24.9	−26.3
		−23.0	−25.4	−23.6	−25.1

five-membered rings than for six-membered rings; this clearly contradicts Brown's views.

It should be borne in mind that not all reactions that involve a change of coordination number can be fitted into the scheme of *I*-strain. The reaction mechanism, which is frequently not known, evidently plays an important part. We have seen that addition to carbonyl groups proceeds according to predictions based on the concept of *I*-strain. It would seem that reactions involving addition to various reagents to C=C double bonds should also proceed faster with six-membered rings than with others (at least for the *cis*-cycloolefins free from Baeyer strain). In fact, just the reverse is observed. If the rate constants for the addition of diethyl aluminium hydride to *cis*-cycloolefins[135] are examined (Table 19), it turns out that the reaction is slowest with six-, ten-, and eleven-membered rings. The same relationship holds for the addition of hexachlorocyclopentadiene to *cis*-cycloolefins[135] (Table 20); in this reaction, the cycloolefin acts as the dienophile.

Similar correlations are encountered in the addition of silver nitrate to *cis*-cycloolefins[136]. Even if the greater reactivity of cyclobutene and cyclopentene can be ascribed to Baeyer strain, the reason for the reactivity of *cis*-cycloolefins with 7–9 atoms in the ring remains obscure.

TABLE 19.



n	4	5	6	7	8	9	10	11
$k_{1,-1} \times 10^4$, min^{-1} at 78°C	180	35	4	65	80	25	3	5

TABLE 20. Addition of hexachlorocyclopentadiene to *cis*-cycloolefins.

n	5	6	7	8	9	10
$k_1 \times 10^4$, min^{-1} at 78°C	90	4	120	300	60	3.7

To sum up, it can be said that the present concept of *I*-strain is not universally applicable and requires a more precise definition. However, it is extremely useful for the systematisation of the various reactions of cyclic compounds and, when other factors (both steric and polar) are taken into account, makes possible successful explanation of certain peculiarities in the chemical behaviour of various cyclic compounds.

3. RING FORMATION AND CLEAVAGE; THEIR RELATION TO STRAIN*

It is well known that ever since the formulation of the Baeyer theory, the idea has taken root of a direct relation between the ease of formation and cleavage of rings, on the one hand, and their strain, on the other. It was supposed that the probability of forming a ring from an acyclic compound and its stability to ring-cleavage reactions were less the greater the strain of the ring. It should be pointed out that at the time when the strain theory was formulated macrocyclic compounds were quite unknown, while the few compounds with three-, four-, and seven-membered rings that had been obtained appeared to be exceptions which only lent support to the general rule that such rings were unstable and tended not to be formed. However, the development of alicyclic chemistry towards the end of the last century and the beginning of the present one revealed the inadequacy of these ideas.

Advances in the synthesis of three- and four-membered rings (the work of G. G. Gustavson and W. Perkin, Jr. should be particularly mentioned) and the work of V. V. Markovnikov in the field of seven-membered rings, made these compounds available, and N. Ya. Dem'yanov's investigations of the isomerisation of cyclic compounds showed that there was no impassable gulf between rings of different size. In spite of the fact that large rings were still unknown, doubts arose in view of the fairly stable nature of seven-membered rings, of the existence of Baeyer "negative strain" in all rings containing more than five atoms.

* Ring formation under the conditions of gas-phase heterogeneous catalysis is beyond the scope of this paper and requires special consideration.

It was mentioned earlier that conformational strain is inherent in seven-membered and intermediate-sized rings, which according to Sachse and Mohr are free of angular strain, and in five-membered rings; this results in an increase of energy content (Table 1). It would be natural to suppose that, like angular strain, conformational strain should exert a definite influence on the stability of rings in various chemical reactions. However, since the rupture of a C–C bond requires an extremely vigorous attack on a molecule, small differences of energy can remain undetected. At the same time, ring cleavage in a number of heterocyclic compounds is generally much easier, and the relation between ease of cleavage and ring size shows more clearly. It must be borne in mind that a direct variation of ease of ring cleavage with strain can only be expected when the ring-cleavage step is the slowest. In general, data about the stability of rings, based on the rates of cleavage, give no indication of the amount of strain. For example, hydrolysis of six-membered lactones and lactams, as was mentioned earlier, is considerably faster than that of the five- and seven-membered compounds. However, it would be wrong to assert in this connection that six-membered rings are more strained than five- or seven-membered rings. The observed relation between rate of hydrolysis and ring size can be explained by the concept of *I*-strain, inasmuch as a change in the coordination number of an atom in the ring occurs in the rate-determining stage of the reaction, while the subsequent ring cleavage proceeds at a faster rate. In certain cases, apparently, there is a direct relationship between the stability and the strain of a ring. This was observed, for example, in an investigation of the thermal dissociation of cyclic polymethyleneureas[137] and of the stability of cyclic disulphides[138]. In general there are no grounds for a connection between the stability and strain of rings. The nature of the relationship between these two factors is, in each instance, determined by the reaction mechanism.

With regard to a relation between tendency to ring formation and ring strain, the regular connection suggested by Baeyer, does not exist. Mohr[8], referring to the unstrained models of higher rings, tried to explain why these unstrained than eight members were unknown). In order to form a ring from an acyclic molecule, the latter must adopt a form suitable for cyclisation, i.e. one in which the reacting groups will be close together. The longer the chain of an aliphatic compound, the more various forms can its molecule adopt by internal rotation (these forms are now called conformations). We cannot, at will, impart to a molecule the necessary form or prevent the presence of forms unfavourable to cyclisation, so that the required form becomes rarer the longer and more mobile the chain between the two end-groups; in other words, the laws of statistics apply. Furthermore, Mohr pointed out that the ease of cyclisation may be affected by the mutual attraction or repulsion of atoms and by the presence or absence of substituents, but he did not deal in detail with this subject. These statements retain their significance to this day.

Making use of modern ideas, one can say that the tendency to ring formation is a complex function of the distance between the reacting groups and the loss of entropy involved in their fixation, of Baeyer strain, Pitzer strain, and the compression of van der Waals radii.

In cyclisation, two reactions are competing: intramolecular–ring formation, and intermolecular–polycondensation or polymerisation. As a rule, the latter reaction is thermodynamically more favourable. Calculation of the change of Gibb's free energy for the hypothetical polymerisation of cycloalkanes to linear polymethylenes, shows that such a process must be accompanied by a diminution of free energy with all rings except five- and six-membered rings (cyclohexane, alkylcyclohexanes, and alkylcyclopentanes)[139]. The same conclusions also apply to heterocyclic compounds[140]. Here, the general nature of the relation between ΔG and ring size is similar to that worked out for the cycloalkanes, particularly if the hetero-atom is not very different from carbon in volume and in the angles between the bonds (e.g. oxygen or nitrogen but not sulphur). Consequently, it may be supposed that the formation of rings, except five- and six-membered ones, involves a smaller gain of free energy than polycondensation and, in the case of reversible reactions, the products of intermolecular condensation should predominate over cyclic compounds in the equilibrium mixture. However, the possibility of cyclisation is not determined only by thermodynamic factors. If the processes are practically irreversible, the nature of the products depends only on the ratio of the rates of the monomolecular cyclisation reaction and the bimolecular reaction of linear dimerisation, which is the first stage of polycondensation, and not on the ratio of the values of ΔG for the two competing reactions. Thus, the greater rate of cyclisation compared to that of dimerisation corresponds to the fact that even the strained three- and four-membered rings are formed fairly easily. At the same time, the unstrained large rings and particularly the little-strained (as far as this can be judged from heats of combustion) intermediate-sized rings were first obtained in very low yields[14]. Apparently for reasons first discussed by Mohr (see above), the rate constant for the formation of macrocyclic compounds is appreciably lower than the rate constant for polycondensation. It is well known that macrocyclic compounds can now be obtained in fairly high yield (see the review by Ziegler[141]); this is accomplished primarily by using high dilution during cyclisation. The principle of high dilution, proposed by Ruggli, was first applied by Ziegler[142]. In conditions of high dilution, the possibility of intermolecular reaction is limited and intramolecular cyclisation becomes more probable. Naturally, the rate of both reactions is reduced, but that of the intermolecular reaction is reduced more than that of the intramolecular. The point is that the rate of the monomolecular reaction is proportional to the concentration of the starting material ($v_1 = k_1 c$) while the rate of the bimolecular reaction is proportional to the square of this concentration ($v_2 = k_2 c^2$). Thus if the rate of the first reaction is decreased 10 times by dilution, that of the second will decrease 100 times*.

The effect achieved by using high dilutions does not generally depend on whether the reaction is reversible or irreversible. In the case of an irreversible reaction, the composition of the products already formed is not changed by extending its duration. In a reversible reaction, thermodynamic equilibrium can, in principle, be achieved, although in practice, because of the retardation of the reaction by the high dilution, a very long time is required for the establishment of equilibrium.

Inasmuch as the height of the activation barrier of any chemical reaction is determined by the change of the free

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* In order not to increase the volume of the reaction mixture unduly, cyclisation reactions are conducted using a special technique of high dilution[141]. In some cases, when the solubility of the substance being cyclised is small and the reaction proceeds in a heterogeneous medium, macrocyclic compounds can be obtained in a small volume of solvent, without using the high dilution technique (see, for example, work by Gol'dfarb and Kondakova[143]).

energy of activation $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$ ($\Delta H^{\#}$ corresponds to the activation energy in the Arrhenius equation, while $\Delta S^{\#}$ — — the entropy of activation — represents the probability of attaining the transition state), one can refer to the enthalpy ($\Delta H^{\#}$) and entropy ($-T\Delta S^{\#}$) barriers of the cyclisation reaction[28].

In the synthesis of unstrained large rings (13 members and greater), the entropy barrier is of prime importance, while in the synthesis of strained small rings, it is the enthalpy barrier. The enthalpy factor is essentially *energetic* in nature: it represents that part of the energy of the transition state that is associated with distortion of valence angles and unfavourable conformations. The entropy factor is associated with the probability of occurrence of the "kinked" form of the chain, favourable to cyclisation, with the functional groups adjacent. The influence of both these factors is clearly manifested in the synthesis of intermediate-sized rings (8–12 atoms in the ring). These rings are the most difficult to obtain by cyclisation, which can be explained by both the small probability of an encounter between the spatially remote end-groups and the non-classical strain of the completed ring.

Although there is no regular relationship between strain and the rate of formation of rings (p. 229), cyclisation is generally easier from certain more favourable types of chain or when an unstrained ring is being formed. For example, exchanging a methylene group in the bifunctional compound for oxygen is generally accompanied by an increase in the yield of cyclic compound (the "oxygen effect"[28,141]); this is due to the diminution of conformational strain when a tetravalent atom is exchanged for a divalent atom. The presence of rigid groups (double bonds, aromatic rings) in the chain of the compound being cyclised, causes a decrease of mobility of the chain and hence of the number of possible conformations. As a result, favourable conformations become more probable and the yield of cyclic compound increases (the "rigid-group principle"[141]*).

The probability of formation of a favourable configuration of the chain also depends on the mechanism of cyclisation. Thus, in the acyloin condensation of esters of dicarboxylic acids, which is carried out in a heterogeneous medium, the probability of approach of the alkoxycarbonyl groups is increased on account of chemisorption on the surface of the molten metallic sodium[26,28].

The probability of cyclisation can be increased by the presence in a bifunctional compound of even quite small side-groups, which limit internal rotation[144]. As a result, the chain can more often adopt a "kinked" conformation with a favourable disposition of the functional groups. As the ratio of the first and second dissociation constants of alkyl-substituted dicarboxylic acids shows, the carboxyl groups are closer together than in the unsubstituted acids[145,146]. In this connection, the very easy formation of the anhydrides of alkyl-substituted glutaric and succinnic acids, which has been known for a long time, can be understood, The presence of substituents in the higher dicarboxylic acids similarly facilitates cyclisation. Thus $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid forms a monomeric anhydride with a seven-membered ring, while under the same conditions, adipic acid gives a polymeric anhydride[147]. Higher $\alpha,\alpha,\alpha',\alpha$-tetramethyl-substituted dicarboxylic acids give dimeric as well as polymeric anhydrides, whereas the corresponding unsubstituted acids give only the latter[148].

The effect of substituents on the ease of cyclisation is due primarily to their volume. This can be clearly seen from the kinetic data on the cyclisation of substituted ω-bromobutylamines[149] (Table 21). Aryl and alkyl groups have opposite inductive effects. Nevertheless, the rates of cyclisation of the diphenyl- and diisopropyl-substituted compounds are not very different.

In general, one can say that the increase in the rate of cyclisation when substituents are introduced, is due primarily to a conformational effect[149]. The substituents promote an increase in the content of the *gauche*-form at the expense of the transoid form; as a result, the reactive groups find themselves in a position where cyclisation is possible.

Bulky substituents, situated near the reactive groups, can increase the probability of cyclisation not only by virtue of their effect on the conformation of the chain, but also because they create steric hindrance to intermolecular reaction. The use of bifunctional compounds with large substituents has made it possible, in a number of cases, to obtain macrocyclic compounds without having to use high dilutions[150,151,152].

The presence of substituents also plays an important part in the production of small rings. There is even a view[153] that, in general, "the presence of substituents and their nature are of greater importance to the ease of closure and the stability of a ring, than the number of atoms making up the ring".

The relative tendencies to cyclisation of bifunctional compounds referred to above can be extremely helpful in considering the processes of polycondensation of bifunctional compounds and polymerisation of heterocyclic compounds important in practical applications.

A vast amount of literature has been devoted to problems connected with the production of high-molecular-weight compounds. Much of this has been generalised in a number of reviews and monographs (see the monograph by Korshak[154] and the literature cited therein). We are at present interested only in the comparative polymerisability of rings of different size and its relation to the probability of formation of ring compounds in polymerisation and polycondensation processes. Certain questions, relating to the thermodynamics and kinetics of polymerisation of cyclic compounds, are dealt with in a recently published review by Dainton and Ivin[155]. The values quoted there, and already referred to, of the change in free energy for the hypothetical polymerisation of cycloalkanes (Fig. 6, see p.224) are of particular interest. From these values, it is possible to conclude, for example, that the polymerisation of cyclohexane and, similarly, methyl- and 1,1-dimethylcyclohexane at 25°, is impossible. It should be emphasised, however, that the fact that a process is thermodynamically possible is no guarantee that it can be realised in practice. At present, there is no known method of polymerising cyclopropane and cyclobutane. 1,1-Dimethylcyclopropane is the only simple cycloalkane that will polymerise comparatively easily, in the presence of aluminium bromide[156]. Polymers can also be obtained from 1,2-dimethyl-, ethyl-, and propylcyclopropanes and from methyl- and ethylcyclobutane, but with these the reaction is much slower. The small tendency of cycloalkanes to polymerise in the presence of a reagent such as aluminium bromide, can probably be explained by the fact that in such conditions other reactions proceed at a fast rate. Turova–Polyak and coworkers[157] (see also the literature

* What has been said concerning the influence of rigid groups, naturally relates to macrocyclic systems and does not apply to compounds with rings of the usual size.

cited by Turova–Polyak[157]) showed that in the presence of aluminium chloride four-, seven-, and eight-membered rings are converted to cyclohexane derivatives. Homologues of cyclopentane, except for methylcyclopentane, are similarly converted to cyclohexane derivatives, while methylcyclopentane forms an equilibrium mixture, containing from 78 to 88% cyclohexane, depending on the temperature. Clearly, if the formation of cyclohexane derivatives proceeds at an appreciable rate, there is little hope of obtaining polymerisation products, since the formation of these from cyclohexane derivatives is thermodynamically impossible.

The polymerisation of many heterocyclic compounds, e.g. lactams, lactones, and anhydrides, can be regarded as an equilibrium process. In a number of cases, it proceeds via a stage in which the corresponding open-chain bifunctional compound is formed[158]. In particular, the polymerisation of caprolactam only takes place in the presence of catalysts, e.g. water, which convert the lactam to ϵ-aminocaproic acid[159,160], which then reacts with another molecule of lactam. The hydrolysis stage is the slowest and determines the rate of polymerisation[161] *. Such processess can be considered together with polycondensation of bifunctional compounds, since the equilibrium mixture can contain the linear monomer (bifunctional compound), the cyclic monomer, and the linear polymer.

The products formed in equilibrium polymerisation reactions depend on the reaction conditions. This statement can be illustrated by a few examples. As early as 1929, Carothers[164] formulated a rule according to which condensation reactions proceed intramolecularly if five- or six-membered rings can be produced thereby; reactions that can lead to seven-membered and larger rings generally proceed intermolecularly and result in polycondensation products. Although seven-membered rings may sometimes be obtained, eight-membered and larger rings are hardly ever found. This rule does not always hold, but it is supported by observations on the polymerisation of lactams in the presence of traces of water: the five-membered γ-butyrolactam and the six-membered δ-valerolactam do not polymerise under these conditions, the seven-membered ϵ-caprolactam partially polymerises (the equilibrium mixture always contains a small amount of monomer), the eight-membered ξ-enantholactam polymerises practically completely[158], while the nine-membered η-caprylolactam and the amino-acids that form 10-, 11-, 12-, and 18-membered lactams all polymerise completely[165].

TABLE 21. Rate of cyclisation of substituted ω-bromobutylamines.

Starting material	Relative cyclisation rate
4-Bromobutylamine	1.00
1,1-Dimethyl-4-bromobutylamine	2.19
2,2-Dimethyl-4-bromobutylamine	158
2,2-Diethyl-4-bromobutylamine	594
2,2-Diisopropyl-4-bromobutylamine	9190
2,2-Diphenyl-4-bromobutylamine	5250
3,3-Dimethyl-4-bromobutylamine	0.158

It might appear that the examples quoted prove the existence of a parallel between strain in rings and their ability to polymerise, although there is, in general, no such relationship. Not infrequently, unstrained rings undergo polymerisation, for example, six-membered* (see the review by Strepikheev[158]), 16-membered[173], and also five-membered rings[173,174,175]. It is interesting to note that α-pyrrolidone, which does not polymerise in the presence of water, polymerises under the influence of alkaline reagents[175]. The seven-membered ϵ-caprolactam[158] and tetramethyleneformal[174], which polymerise to the extent of 80–90% without a solvent, do not polymerise at all in 5–10% solution. Evidently, even a relatively small dilution (compared to that used in the synthesis of macrocycles), is sufficient for the preferential formation of the seven-membered ring, as against the polymer.

The equilibrium

cyclic monomer $\rightleftharpoons$ linear monomer $\rightleftharpoons$ linear polymer

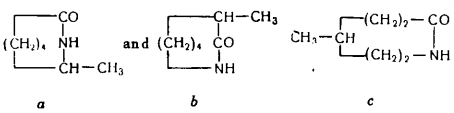
can also be shifted, without the use of dilution, towards formation of the cyclic monomer, if this is removed from the equilibrium mixture. In this way one can obtain the monomeric and dimeric cyclic anhydrides of the higher dicarboxylic acids[176], cyclic esters of glycols and dicarboxylic acids[177,178], and the higher lactones[179]. It has been suggested that the pyrolysis (after Ružicka) of the salts of di-

* However, one cannot conclude from this that the polymerisability of a ring is greater, the faster the hydrolysis rate. The formation of an amino-acid from a lactam may proceed easily, but if the amino-acid does not subsequently react with a molecule of lactam or with another molecule of amino-acid, polymerisation products of the lactam cannot be formed at all. Carothers[162] once suggested a parallel between polymerisability and hydrolysis rate of cyclic monomers. In recently published work[163], Hall, Brandt, and Mason showed that this was rarely justified and could not be called a general rule. It may be noted that, while the rate of hydrolysis of α-piperidone is greater than that of α-pyrrolidone, the polymerisabilities are in the reverse order; similarly, propiolactone polymerise readily, while γ-butyrolactone does not polymerise, although they hydrolyse at comparable rates.

* From the heats of combustion (in the liquid state) of 5- to 8-membered lactams, determined in the Thermal Laboratory at the University of Moscow[166], the authors concluded that even the 6-membered α-piperidone is strained, and to a greater extent than the 5-membered α-pyrrolidone. This conclusion clearly contradicts all the data on the strain of cyclic compounds. If the possibility of experimental error is excluded, it may be that in piperidone, compared to other lactams, the tautomeric lactim-lactam equilibrium is displaced in the direction of the endocyclic lactim form, and that the experimental value of the heat of combustion should not be compared with the value calculated for the lactam form, but with that for the lactim form (or with a mixture of the two). However, an infra-red spectroscopic study shows that the lactim form is not present in the lactams that have a ring containing from the 5-membered α-pyrrolidone. This conclusion clearly contradicts molecular interaction, which, as spectral data[168] and dipole-moment measurements[169] show, is extremely powerful in lactams. To exclude the influence of molecular interaction, it would be of very great interest to determine heats of combustion of lactams in the gaseous, instead of the liquid, state. The heats of combustion of alkyl-substituted lactams[170] and *N*-methyllactams[171], determined in the same laboratory of the University of Moscow, clearly indicate the lack of strain in a 6-membered ring. The heats of combustion of cyclic ketones[172], which are steric analogues of lactams, show that, in this case too, the 6-membered ring is unstrained.

carboxylic acids, is also a reversible reaction and that the formation of macrocyclic ketones is due to removal of one of the components of the equilibrium mixture[18].

As would be expected, when substituents are present in a molecule of cyclic monomer polymerisation is hindered[132,144,162,180]; the proximity of a substituent to the reaction centre is of the greatest importance. Thus, of the isomeric methylcaprolactams that have been studied[144], the slowest to polymerise is the mixture of ϵ-methyl-ϵ-caprolactam (*a*) and α-methyl-ϵ-caprolactam (*b*), obtained by the Beckmann rearrangement of the oxime of *o*-methylcyclohexanone, while the fastest is the γ-methyl-ϵ-caprolactam (*c*):



a *b* *c*

N-methylcaprolactam, and also a number of other *N*-substituted caprolactams, do not polymerise at all[181,182]; neither do dialkyl-substituted caprolactams[182,183]. At the same time, no difficulties are encountered in the polycondensation of 10-aminoundecanoic[184] and *N*-methyl-11-aminoundecanoic[185] acids. Apparently, the formation of 11- and 12-membered rings is so improbable that it need not be considered, even when the bifunctional molecule is branched; a seven-membered lactam is formed readily, without dilution, when the molecule of ϵ-aminocaproic acid contains one alkyl substituent on the nitrogen atom or two on carbon atoms[182].

For all the above reasons, one cannot agree with the statement by Hall and his collaborators[163]: "Polymerisability of a cyclic derivative is an indication of strain in the ring." They refer, in particular to the work of Dainton and Ivin[155], although it contains data which contradict their thesis. It seems to us, that the material that has been discussed enables one to conclude that, in general, the ability of a cyclic compound to polymerise is no indication of its strain. In particular, the example of the equilibrium polymerisation of heterocyclic compounds shows that in such reactions certain general rules, discussed above, play an important part, determining both the course of polymerisation and the processes of cyclisation.

CONCLUSION

Introduction of electronic concepts into chemistry led to the widespread use of polar effects in the interpretation of the reactivity of organic compounds. It is hardly necessary to stress the importance of these ideas, which played a prominent part in the development of the modern structure of organic chemistry. At the same time it should be noted that excessive enthusiasm for polar effects and attempts to ascribe every occurrence to the interaction of charges arising or existing in a molecule, led to the neglect or underestimation of several other factors that frequently play a decisive part in the development of a chemical reaction. This applies particularly to the spatial "shape" of a molecule, which is usually considered in connection with so-called steric hindrance. The influence of this factor on chemical behaviour was noted by Kehrmann, V. Meyer, N. A. Menshutkin, and others before the end of the last century, and for many years served as one of the means of interpreting the reactivity of organic compounds. However, around the 1940's, owing to the efforts to fit everything into the frame of one electronic concept, an extraordinary scepticism became widespread, concerning the role of the steric effect in chemical behaviour. The well-known books by Hammett and Remick hardly consider the steric effect. Moreover, as Brown[87] remarks, the steric effect is sometimes regarded as a meaningless concept: "Steric hindrance.... has become the last refuge of the puzzled organic chemist" states Ray in his textbook of organic chemistry (quoted from Brown[87]). Such a statement does not need to be refuted, but the importance of steric factors in a fairly wide range of chemical reactions still requires to be evaluated. At the present time, there is no generalised theoretical basis for this purpose, but several valuable facts and opinions may be gleaned from the book "Steric Effects in Organic Chemistry" (see Dauben and Pitzer[25] and other chapters in this book). To a certain extent, the present review may serve as a similar source of data in the limited field of cyclic compounds. In fact, ideas about strain, both as developed by Baeyer and also the very latest, are concerned primarily with the relative disposition in space of separate parts of a molecule, and enable one to clarify the bearing of these purely steric factors on the reactivity of a chemical compound. As we have seen already, peculiarities in those reactions of cyclic compounds not involving ring cleavage, which are best described in terms of the steric effect, have been increasingly studied in recent years. Of course, the steric effect cannot explain all the diverse reactions of cyclic systems. In this connection, we should like to emphasise again that in considering specific chemical problems it is essential to take various effects into account (polar, steric, solvation, etc.), each of which may, in one case or another, be of decisive importance. Although an accurate appraisal of the influence of all the factors is not possible at present, methods exist which make it possible, by analogy and by consideration of molecular models, to make an approximate estimate of their importance*.

The steric effect is caused by interaction of the outer electron shells of non-bonded atoms and, consequently, it is based, as is the polar effect also, on forces that are electrical in nature. However, steric interaction decays exponentially with distance; its nature is far from clear and this is one reason why the importance and the role of steric factors are still largely unknown. At the same time, it is evident enough that further study of their role in chemical reactions, linked with new advances in the modern electronic theory is a necessary condition for the progress of organic chemistry.

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* Of course, an appraisal of the reactivity of a compound is inevitably linked with certain assumptions relating to the transition state; this can be seen both from the material discussed and from the fairly numerous data concerning acyclic compounds (see for example, Bergel'son[21]).

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Organic Chemistry

THE RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS OF INORGANIC NITROGEN COMPOUNDS

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The radiolysis of solutions of inorganic nitrogen compounds is an extremely complex and important problem in radiochemistry owing to the multiplicity of the valency states of nitrogen and the comparative ease of their mutual interconversion. Although a great deal of work has been done on the mechanism of the radiolytic reactions of nitrogen compounds in solution, much remains obscure.

1. NITROGEN FIXATION INDUCED BY IONISING RADIATION IN THE PRESENCE OF WATER

Orekhov et al.[1-3] found that on irradiating a KOH solution with Co^{60} γ-rays in the presence of oxygen, the nitrite formed and the equivalent quantity of nitrate increased linearly with the dose. The G value* for the nitrogen entering into combination was about 0.2 atoms. Increasing the air pressure on the solution (up to 25 atm) had no appreciable effect on G. They considered that this reaction depends on the reaction of free OH radicals, formed by the radiolysis of water, with free molecules of nitrogen, simultaneously with atomic hydrogen or the radical HO_2:

$$OH + N - N + HO_2 \rightarrow NOH + HNO_2. \quad (1)$$

This reaction of nitrogen was not observed in acid solutions.

Primak and Fuchs irradiated a mixture of nitrogen and oxygen with a nuclear reactor in the presence of nickel or other metals in a quartz ampoule. No products were formed with dry gases. A significant quantity of $Ni(NO_3)_2 \cdot 6H_2O$ was produced when air at 1 atm was saturated with water at 28°. The yield of bound nitrogen, G, was about 3 atoms, but the accuracy of the determinations was not high.

Wright et al.[5] studied the formation of HNO_3 from air and nitrogen irradiated over water in a nuclear reactor. G (HNO_3) was about 1 molecule (calculated from the energy absorbed by the gases).

Dmitriev and Pshezhetskii[6,7] found that G was 0.2 atoms for the oxidation of nitrogen at atmospheric pressure over water by 200 keV electrons. The reaction proceeded essentially at the expense of the energy absorbed in the gaseous phase.

Jones[8] found that nitric acid and nitrous oxide were formed by a beam of fast electrons (1 MeV) acting on a nitrogen–oxygen–water system. With high integral doses (using up all the water vapour present in the mixture) the HNO_3

* In this and all subsequent cases, G is the amount of radiolytic reaction (in molecules, atoms, ions, etc.,) per 100 eV of energy absorbed.

formed decomposed, giving a corresponding quantity of NO_2. Jones showed that the yield depended on the oxygen concentration reaching a maximum with 15.4 mole % of oxygen, in contrast to the conclusion of Wright et al.[5].

2. RADIOLYSIS OF AMMONIA, HYDRAZINE, AND HYDROXYLAMINE SOLUTIONS

Rigg et al.[9] found that nitrites were formed by the radiolysis of ammonia solutions in the presence of oxygen. The yield depended largely on the mean pH and free-ammonia concentration, which was determined by the equilibrium

$$NH_3 + H^+ \rightleftharpoons NH_4^+. \quad (2)$$

The maximum value of G for NO_2^- was ~1.3 ions. There was no difference between the behaviour of $(NH_4)_2SO_4$ solutions saturated with air or oxygen, but in degassed solutions ammonia was not oxidised. The following mechanism was suggested:

$$NH_3 + OH \rightarrow NH_2 + H_2O, \quad (3)$$

$$NH_2 + O_2 \rightarrow NH_2O_2, \quad (4)$$

$$NH_2O_2 + OH \rightarrow HNO_2 + H_2O. \quad (5)$$

The radical NH_2 can undergo disproportionation:

$$2NH_2 \rightarrow NH_3 + NH. \quad (6)$$

The radical NH is unstable and breaks up into NH_3, N_2, and possibly H_2. This explains the absence of oxidation products on irradiating ammonia solutions in vacuo. The reaction in the presence of oxygen is

$$NH + O_2 \rightarrow HNO_2, \quad (7)$$

with the direct formation of nitrous acid.

According to Sharpatyi et al.[10] irradiation of an ammonia solution (0.15 M; pH 14), saturated with nitrogen, in the presence of 1 M $NaNO_3$ by Co^{60} γ-rays produced nitrite with $G(NO_2^-) = 6$ ions. In the absence of $NaNO_3$ but with oxygen present, $G(NO_2^-) = 1.5$ ions, as Rigg et al. found[9]. Proskurnin et al.[10,11] explained the increase in $G(NO_2^-)$ in solutions containing $NaNO_3$ by the occurrence of the following reactions:

$$9OH + 1.5NH_3 + 1.5OH^- \rightarrow 1.5NO_2^- + 7.5H_2O, \quad (8)$$

$$9H + 4.5NO_3^- \rightarrow 4.5NO_2^- + 4.5H_2O. \quad (9)$$

$1.5NO_2^-$ ions are formed in reaction (8) while reaction (9) forms $4.5NO_2^-$ ions; thus the total yield amounts to 6 ions/100 eV. Reaction (8) takes place in the absence of $NaNO_3$, but with oxygen present, giving $G(NO_2^-) = 1.5$ ions. Proskurnin et al. consider that the role of oxygen is merely to render the H atoms inactive. Thus neither the HO_2 radical, nor other radicals, nor hydrogen peroxide (in alkaline solutions) take part in the oxidation of ammonia. According to Eqn. (9), nine molecules of water, dissociated by radiolysis, must be used in the oxidation of ammonia, which is evidence for the participation of ionised and excited water molecules in the reaction.

Dewhurst and Burton[12] studied the conversion of hydrazine solutions by Co^{60} γ-rays. They found that the yields of products in air-free solutions were independent of the hydrazine concentration greater than 2×10^{-2} M, and were $G(-N_2H_4) = G(NH_3) \cong 5.2$ and $G(N_2) = G(H_2) = 2.5$. However, the yields fall appreciably in more dilute solutions. Saturation with hydrogen and the addition of $(NH_4)_2SO_4$ (0.02 M) or KBr (10^{-4} to 10^{-3} M) does not alter the value of G to any extent. $G(H_2) = G(N_2)$ when pH lies between 0.3 and 12.3, and $G(NH_3) = 2G(N_2) \cong G(-N_2H_4)$ in this range. The yields are practically constant up to pH 8 but fall appreciably at higher values. The H and OH radicals formed during the radiolysis of water are assumed to react with acidified hydrazine as follows:

$$N_2H_4 + H^+ \rightarrow N_2H_5^+, \quad (10)$$

$$N_2H_5^+ + H \rightarrow H_2 + N_2H_4^+, \quad (11)$$

$$N_2H_5^+ + OH \rightarrow H_2O + N_2H_4^+, \quad (12)$$

$$N_2H_4^+ + \text{water} \rightarrow N_2H_3 + H^+(aq), \quad (13)$$

$$2N_2H_3 \rightarrow N_4H_6, \quad (14)$$

$$N_4H_6 \rightarrow N_2 + 2NH_3. \quad (15)$$

The diminution in yield at low hydrazine concentrations is explained by competition between reactions (11) and (12) and the recombination reaction of H and OH. In more concentrated solutions (above 2×10^{-2} M) the H and OH radicals are largely consumed by the decomposition of hydrazine.

Cottin and Lefort[13] found that in the radiolysis of hydrazine sulphate solutions by Po^{210} α-particles $G(H_2)$ was independent of hydrazine concentration between 10^{-4} and 10^{-2} M, and was equal to 1.6 molecules. Lefort and Haissinsky[14] treated hydrazine solutions with Co^{60} γ-rays and Po^{210} α-particles. As Dewhurst and Burton found[12], the yield with γ-rays depended on concentration and pH and the radiolysis was believed to occur at the expense of H and OH radicals. The yield with α-particles was significantly lower, giving, for a 2×10^{-3} M solution in 0.1N H_2SO_4, $G(-N_2H_4) = 1.0$, $G(N_2) = 0.55$, and $G(NH_3) = 0.9$, while γ-rays, acting on a 10^{-3} M solution, gave $G(-N_2H_4) = 2$ and $G(N_2) = 2.2$. The action of α-particles on acid solutions produced also hydrogen peroxide and oxygen, which were not found after γ-irradiation. This is explained by the following reactions:

$$N_2H_4 + OH \rightarrow N_2H_3 + H_2O \rightarrow \tfrac{1}{2}N_2 + NH_3 + H_2O, \quad (16)$$

$$OH + OH \rightarrow H_2O_2, \quad (17)$$

$$2H_2O_2 + N_2H_4 \rightarrow N_2 + 4H_2O, \quad (18)$$

$$H_2O_2 + OH \rightarrow HO_2 + H_2O, \quad (19)$$

$$HO_2 + OH \rightarrow H_2O + O_2. \quad (20)$$

Lefort and Tarrago[15] found that ammonium ions, nitrogen, hyponitrous acid ($H_2N_2O_2$), and hydrogen were produced by Co^{60} γ-rays acting on a hydroxylamine sulphate solution (concentration 5×10^{-3} M) in the absence of air. The yield was $G(-NH_2OH) = 6.8 \pm 0.2$, $G(NH_4^+) = 2.25 \pm 0.1$, $G(N_2) = 2.0 \pm 0.05$, $G(H_2N_2O_2) = 0.33 \pm 0.05$, and $G(H_2) = 0.45 \pm 0.2$. The following mechanism was suggested*:

$$NH_3OH^+ + H \rightarrow H_2O + NH_3^+ \text{ (or } NH_2), \quad (21)$$

$$NH_2 + NH_3OH^+ \rightarrow NH_4^+ + ONH_2, \quad (22)$$

$$NH_3OH^+ + OH \rightarrow H_2O + ONH_3^+ \text{ (or } ONH_2), \quad (23)$$

$$2ONH_2 \rightarrow N_2 + 2H_2O, \quad (24)$$

$$H_2O_2 + ONH_2 \rightarrow NO + 2H_2O, \quad (25)$$

$$NO + ONH_2 \rightarrow H_2N_2O_2, \quad (26)$$

$$NO + NH_2 \rightarrow N_2 + H_2O. \quad (27)$$

In the presence of oxygen nitrate ions are formed.

* The pH of solution was about 4.0; in these conditions hydroxylamine exists as NH_3OH^+.

TABLE 1. Yield of hydrogen and nitric oxide on irradiation of aqueous KNO_2 with Co^{60} γ-rays (from Schwarz [20]).

Concentration of KNO_2, M	$G(H_2)$, molecules/100 eV	$G(NO)$, molecules/100 eV
$4 \cdot 10^{-5}$	0.440	—
$1.2 \cdot 10^{-3}$	0.408	—
$1.6 \cdot 10^{-2}$	0.356	—
$5.8 \cdot 10^{-2}$	0.320	—
0.165	0.298	0.026
0.394	0.226	0.081

3. RADIOCHEMICAL OXIDATION OF NITRITE TO NITRATE

In 1935 Fricke and Hart [16] were the first to observe that nitrite in a deaerated solution was oxidised to nitrate by X-rays, with the simultaneous evolution of the equivalent quantity of hydrogen. $G(NO_3^-)$ was ~0.7 ion and was independent of the initial nitrite concentration between 5×10^{-5} and 10^{-1} M, and of pH between 2 and 11.

Haissinsky and Lefort [17] showed that sodium nitrite was oxidised to nitrate by X-rays and Po^{210} α-particles. Lefort [18] found that, in the absence of oxygen, the initial yield for the oxidation in 10^{-3} M KNO_2 at pH 6 was 1.75 molecules for X-rays and 0.4 molecule for α-particles.

In a more detailed investigation, Schwarz and Allen [19] found that irradiation of an air-free solution of KNO_2 by X-rays or γ-rays resulted initially mainly in the formation of molecular hydrogen and hydrogen peroxide. The subsequent reaction between the nitrite and the peroxide formed nitrate. The main peculiarity is the competition between reactions (29) and (30)*:

$$H_2O \rightarrow H_2,\ H_2O_2,\ H,\ OH,$$

$$OH + NO_2^- \rightarrow NO_2 + OH^-, \quad (28)$$

$$H + NO_2^- \rightarrow NO + OH^-, \quad (29)$$

$$H + H_2O_2 \rightarrow OH + H_2O, \quad (30)$$

$$NO + NO_2 + H_2O \rightarrow 2HNO_2, \quad (31)$$

$$2NO + H_2O \rightarrow HNO_2 + H^+ + NO_3^-. \quad (32)$$

$G(H_2O_2)$ falls rapidly as the nitrite concentration increases to 2×10^{-3} M and becomes almost constant for concentrations between 10^{-3} and 10^{-2} M. In nitrite solutions containing air or oxygen, the increase of $G(-NO_2^-)$ with increase of the ratio of nitrite concentration to oxygen concentration follows the empirical equation

$$-1/G(-NO_2^-) = (0.87 \pm 0.08) + (1.09 \pm 0.06)[O_2]/[NO_2^-]. \quad (33)$$

Schwarz [20] found that $G(H_2)$ decreased with increase of KNO_2 concentration (see Table 1). Nitric oxide was formed in concentrated solutions of KNO_2; $G(NO) \cong 0.01$ to 0.1 molecule.

According to Orekhov et al. [1-3] the oxidation of KNO_2 in aqueous solution with Co^{60} γ-rays may be expressed by the following equation

$$C_E = C_0 e^{-kE},$$

where C_0 is the initial nitrite concentration and C_E is its concentration after the absorption of energy E. The constant k decreases with increase of pH. They consider that the oxidation is a result of the reaction between NO_2^- ions and OH and HO_2 radicals formed during the radiolysis of water.

Schwarz and Salzman [21], who studied the formation of H_2O_2 during radiolysis of KNO_2 solutions up to 10^{-1} M, found that $G(H_2O_2)$ decreased with increase of concentration, giving 0.62 molecule with 2.3×10^{-4} M and 0.42 with $9.6 \times \times 10^{-2}$ M. They suggest that the mechanism described above [19] should be supplemented by the following reaction:

$$H + NO_3^- \rightarrow NO_2 + OH^-. \quad (34)$$

4. RADIOLYTIC REACTIONS IN AQUEOUS NITRATE AND NITRIC-ACID SOLUTIONS

Many foreign and Soviet workers have studied the radiochemistry of nitrates in aqueous solution. Nitrite ions, hydrogen, oxygen, hydrogen peroxide, nitrogen, and nitrous and nitric oxides are formed on radiolysis.

Yield of Nitrite

Published data about the yield of nitrite (the main product of radiolysis of aqueous nitrates) is given in Table 2. It is seen that $G(NO_2^-)$ increases with increase of nitrate concentration and decrease of acidity, and with rise of temperature and addition of glycerine or glucose to the solution.

According to Kabakchi et al. [28], the nature of the cation as a rule has no significant effect on $G(NO_2^-)$. $G(NO_2^-)$ reaches a definite limit with increase of solute concentration only in solutions of nitrates with the strongly hydrated lithium and beryllium cations. If the concentration is increased further, $G(NO_2^-)$ decreases noticeably and tends to the value for the solid salt, as very strong solutions of $LiNO_3$ and $Be(NO_3)_2$ have structures similar to the solids.

Ryabchikova et al. [33] found that $G(NO_2^-)$ was negligible in silver nitrate solutions. The main product was metallic silver. The yield depended on concentration and was 0.55,

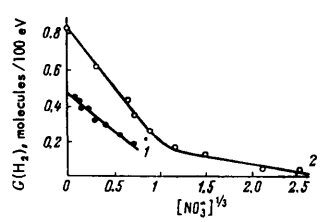


Fig. 1. Dependence of $G(H_2)$ on the concentration of NO_3^- ions in the solution: 1) irradiation of $NaNO_3$ solutions [37] by Co^{60} γ-rays; 2) irradiation of $Ca(NO_3)_2$ solutions with a mixed beam of neutrons and γ-rays [38].

* It was found that in the $KNO_2 - H_2O_2$ system, the ratio of the velocity constants of reactions (29) and (30) is 0.47 ± 0.03.

TABLE 2. Yield of nitrite ions (ions /100 eV) on radiolysis of nitrate solutions.

Salt irradiated	Salt concentration, M	Type of radiation	Dose rate, eV ml^{-1} sec^{-1}	Conditions of irradiation	$G(NO_2)$, ions/100eV	Reference
KNO_3	10^{-2}	X-rays (105 kV)	—	in the presence or absence of air	0.6—0.9	22
KNO_3	10^{-3} 10^{-3}	X-rays Po^{210} α-particles	—	in the absence of air	0.8 0.18	18
KNO_3	0.01 0.1 1.0	Co^{60} γ-rays	$\sim 1.5 \cdot 10^{15}$	in the presence of air in neutral solutions	$\sim$2.0 (initial yield)	1—3
KNO_3	1.0		$\sim 1.5 \cdot 10^{15}$	solution contained 1 M KOH and 10^{-2} M glucose	$\sim$6.0	1—3
$NaNO_3$	0.012 0.1 1.0 3.0	X-rays (90 kV)	up to $\sim 10^{16}$	pH = 6.5; solutions saturated with oxygen	1.0 1.3 2.0 3.3	23
$NaNO_3$	1.0		up to $\sim 10^{16}$	solutions saturated with oxygen, pH = 0.5 pH = 1.5 pH = 2.2 pH = 6.5 pH = 8.4—13	0 0.9 1.6 2.0 2.4	23
$NaNO_3$	1.0	(50 kV)	$1 \cdot 10^{15}$	neutral solution saturated with nitrogen	2.2	24
$NaNO_3$	1.0	Co^{60} γ-rays	$1.1 \cdot 10^{15}$ $1.1 \cdot 10^{15}$	in alkaline solution in the presence of air between 20 and 25° 40° 80°—90° solutions contained 1 M KOH and 10^{-3} to 10^{-1} M glycerine; in the presence of air	1.5—1.8 $\sim$3.3 $\sim$4.0 $\sim$5.8	25, 26
$NaNO_3$	1.0	Co^{60} γ-rays		less than 2.5×10^{-4} M glycerine solution contained air, 1 M KOH, 10^{-3} M glycerine; at 35° 80°—90° solution contained 1 M KOH saturated with nitrogen solution contained 1 M KOH and 2.3×10^{-3} M glycerine; saturated with nitrogen	$\sim$1.6 $\sim$0.4—0.5 $\sim$4.5—4.8 $\sim$4.5—4.8 $\sim$5.3—5.8	25, 26
$Ca(NO_3)_2$	0.1—10.0	U^{235} fission products	—	solution at ~ 80°	very small	27
KNO_3	0.01	Co^{60} γ-rays	$\sim 1.4 \cdot 10^{10}$— $-3 \cdot 10^{14}$	neutral solutions saturated with air (Griess reagent present)	0.53	28, 29
KNO_3	0.1 1.0 2.0 0.01	P^{32} β-rays	$\sim 1.4 \cdot 10^{10}$— $-3 \cdot 10^{14}$ —	neutral solutions saturated with air or nitrogen (Griess reagent present) neutrol solutions saturated with air (Griess reagent present)	2.42 4.09 4.5 0.56	28, 29
	0.1 1.0 0.1 2.0	Pu^{239} α-particles	— —	neutral solutions saturated with air or nitrogen (Griess reagent present)	2.28 4.02 1.2 3.4	
$NaNO_3$	2.0—6.0	Co^{60} γ-rays	—	neutral solutions, saturated with air (Griess reagent present)	4.5	28
KNO_3	2.0—6.0				4.5	
NH_4NO_3	2.0—6.0				4.5	28
$Sr(NO_3)_2$	1.0—3.0				4.5	
$Ba(NO_3)_2$	1.0—3.0				4.5	
$Pb(NO_3)_2$	1.0—3.0		—		4.5	
NiO_3	2.0 $\sim$4.0 $\sim$5.0 $\sim$6.0				4.8 5.1—5.2 5.2—5.3 3.6—3.7	
$Be(NO_3)_2$	$\sim$0.5 $\sim$1.0 2.5 0.1			cooled to temperature of liquid nitrogen	4.6 5.1 3.3 0.2	
$NaNO_3$	1.0 3.0 and 5.0				0.8 1.4	30
$Th(NO_3)_4$	$\sim$0.2—2.7	U^{235} fission products mixed beam of neutrons and γ-rays		between 20° and 300°	insignificant	31
$Ca(NO_3)_2 \cdot 4H_2O$	$\sim$10 for NO_3^-	Co^{60} γ-rays		fused crystalline hydrate	0.5—0.75	32

3.7, and 5.95 atoms/100 eV for 0.1, 0.5, and 1 M solutions respectively. The almost total absence of nitrite ions can be explained either by reaction of Ag^+ with OH radicals, forming Ag^{2+} ions which subsequently oxidise the nitrite ions, or by the direct action of the OH radical on the nitrite. The possibility that Ag^{2+} ions are formed in $AgNO_3$ solutions

was pointed out by Sworski[34]. Thus the nature of the cation has no appreciable effect on $G(NO_2^-)$ only when it cannot undergo oxidation or reduction by the products of radiolysis of water.

The data published about the effect of the nature of the saturating gas on $G(NO_2^-)$ are conflicting. According to Proskurnin et al.[25,35] $G(NO_2^-)$ for 1 M $NaNO_3$ saturated with nitrogen is about $2\frac{1}{2}$ times greater than when saturated with air. Furthermore, the radiolytic reduction of nitrate does not depend on temperature between -10° and 90° if the irradiation is carried out in an inert gas[36]. If the solution is saturated with air, then $G(NO_2^-)$ is strongly temperature-dependent in this range. On the other hand, Kabakchi et al.[28,29] found that the nature of the saturating gas had no effect on $G(NO_2^-)$ at nitrate concentrations above 0.1 M, though in dilute solutions saturated with air or oxygen $G(NO_2^-)$ was somewhat lower than when saturated with nitrogen. According to Bakh[24], this is due to competing reactions of NO_3^- and the molecular oxygen present with atomic hydrogen.

With high-energy radiation (α-particles, recoil protons, and U^{235} fission products*), $G(NO_2^-)$ is appreciably lower than with low-energy radiation.

Yield of Hydrogen

Hydrogen is another product of the reduction of nitrate solutions. Bakh et al.[24] found that $G(H_2)$ decreased with increase of nitrate concentration, giving 0.5, 0.18, and 0.05 molecules respectively for 0.1, 1.0, and 5 M solutions of $NaNO_3$ irradiated with X-rays (dose 10^{15} eV $ml^{-1}sec^{-1}$), and saturated with nitrogen.

Mahlman and Boyle[37] treated nitrate solutions with Co^{60} γ-rays and found that $G(H_2)$ was a function of the cube root of the molar nitrate-ion concentration (Fig. 1, curve *1*). The empirical equation to the curve is

$$G(H_2) = 0.46 - 0.40[NO_3^-]^{1/3}. \quad (35)$$

Sowden[38] treated aqueous $Ca(NO_3)_2$ solutions, between 0.037 M and 15.9 M, with mixed radiation from a reactor and noticed a similar dependence on nitrate concentration. From curve *2* (Fig. 1) it is seen that the relationship between $G(H_2)$ and $[NO_3^-]^{1/3}$ is linear until the nitrate-ion concentration is approximately unimolar, and can be expressed by an equation of the type

$$G(H_2) = A - k[NO_3^-]^{1/3}. \quad (36)$$

The parameter k = 0.65 represents the probability of reaction between the solute and H or OH radicals. The constant A = 0.84 is the hypothetical hydrogen yield at zero concentration.

Decrease of $G(H_2)$ with increase of nitrate concentration was also observed with $UO_2(NO_3)_2$ [39,40] and $Th(NO_3)_4$.[31] Sowden and Lynde[27] found that the relationship between $G(H_2)$ and $Ca(NO_3)_2$ concentration after exposure to U^{235} fission products can be expressed by an equation similar to (36), as was also found for γ-rays and a mixed stream of neutrons and γ-rays. The values of the parameters A and k are 2.0 and 0.8 respectively.

$G(H_2)$ for U^{235} fission products and neutrons is appreciably higher than for γ-rays and X-rays. The high concentration of H atoms in the path of the recoil nuclei from

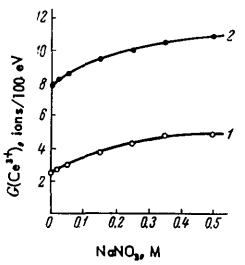


Fig. 2. Influence of $NaNO_3$ in the reduction of Ce^{4+} in 0.8 N H_2SO_4; initial concentration of $Ce^{4+} = 4 \times 10^{-4}$ M (from Sworski[45]): 1) in absence of Te^+; 2) in presence of 2×10^{-3} M Tl^+.

TABLE 3. Dependence of $G(H_2O_2)$ and $G(O_2)$ on concentration of $NaNO_3$ solution (dose rate 10^{15} eV ml^{-1} sec^{-1}; from Bakh et al.[24]).

$NaNO_3$, M	$G(H_2O_2)$	$G(O_2)$	$G(\Sigma$ oxidation equiv.)
0.1	1.60	0.07	3.48
1.0	1.77	0.47	5.42
5.0	1.66	1.45	9.12

U^{235} fission products and of the recoil protons, caused by the passage of fast neutrons through water, increases the probability of recombination processes and the formation of molecular products.

According to Sharpatyi et al.[41], $G(H_2)$ for a 1.0 M solution of $NaNO_3$ is 0.06 molecule (Co^{60} γ-rays) and falls to 0.04 molecule in the presence of 10^{-3} M glycerine.

Thus the decrease in $G(H_2)$ with increase of nitrate concentration is typical for all forms of radiation, and is explained by reaction (34).[23]

Formation of Nitrogen and its Oxides

The formation of nitrogen and its oxides is observed when nitrate solutions are subjected to radiation with high density of ionisation. Bidwell et al.[39] treated uranyl nitrate solutions with U^{235} fission products and found that $G(N_2)$ decreased with increase of $UO_2(NO_3)_2$ concentration; $G(N_2)$ was 0.004 molecule for a solution 1 M in nitrate.

Boyle and Mahlman[31] treated thorium nitrate solution with U^{235} fission products and a mixed beam of neutrons and γ-rays and found that $G(N_2)$ was independent of temperature between 20° and 300°, but depended on the type of radiation and increased with increase of concentration. $G(N_2)$ for a 2.73 M solution was 0.06 molecule for U^{235} fission products, 0.006 for mixed fast neutrons and γ-rays, and 0.001 for γ-rays alone. They consider that the formation of nitrogen results from the direct action of the radiation on the nitrate. This is supported by the fact that $G(N_2)$ is independent of pH and tends to zero at a concentration of about 0.2 M. Oxides of nitrogen, mainly N_2O, were also found.

* U^{235} fission products are streams of recoil nuclei which cause a very high density of ionisation in their path.

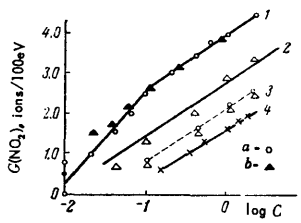


Fig. 3. Dependence of $G(NO_2^-)$ on KNO_3 concentration: 1) with Co^{60} γ-rays (*a* solutions saturated with air; *b* solutions saturated with nitrogen)[28,29]; 2) with Pu^{239} α-particles[28,29]; 3) calculated curve[28,29]; 4) direct action of Co^{60} γ-rays[47].

TABLE 4. Yields for radiolytic reduction of AmO_2^{2+} in acid solutions (from Zaitsev et al.[44]).

H_2SO_4, M	$G(-AmO_2^{2+})$	$HClO_4$, M	$G(-AmO_2^{2+})$	HNO_3, M	$G(-AmO_2^{2+})$
0.1	4.04	0.2	4.04	0.5	7.1
1.0	2.85	2.0	3.20	3.0	8.9
2.0	2.50	4.0	3.20	6.0	9.0
4.0	2.02	6.0	3.40	9.0	10.6
6.0	1.80	4M $HClO_4$ +			
10.0	2.20	+ 2M $NaClO_4$	3.55	14.3	6.0

According to Sowden[38] $G(N_2)$ was $(3.2 \pm 0.6) \times 10^{-3}$ molecules on irradiating 9.4 M $Ca(NO_3)_2$ with mixed fast neutrons and γ-rays from a reactor.

Molecular nitrogen[27] is also formed by the action of U^{235} fission products on $Ca(NO_3)_2$ solutions between 0.2 and 10 M. In the 10 M solution $G(N_2)$ is ~0.09 molecule/100 eV. Below 4 M the relationship between $G(N_2)$ and concentration may be expressed by the empirical equation

$$G(N_2) = 0.004[NO_3^-]^{1/4}. \quad (37)$$

Nitrous oxide was found among the products formed from concentrated $Ca(NO_3)_2$.

Oxidation Products

Oxygen and hydrogen peroxide are among the oxidation products of nitrate solutions. The formation of oxygen has been observed by several authors[24,41]. According to Bakh et al.[23,24], hydrogen peroxide is formed by treating $NaNO_3$ solutions with X-rays, but Sowden and Lynde[27] did not find peroxide in $Ca(NO_3)_2$ solutions treated with U^{235} fission products.

Increase of pH to about 8 caused an increase of $G(H_2O_2)$ but G remained constant when the pH was raised further[23]; a similar relationship was observed for NO_2^- (see Table 2). In Bakh's view the decrease in $G(NO_2^-)$ and $G(H_2O_2)$ is explained by the non-radiolytic reaction

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O, \quad (38)$$

and also by the radiochemical reaction between NO_2^- and H_2O_2, described by Allen and Schwarz[19]. The nature of the saturating gas had an effect on $G(H_2O_2)$ only in dilute solutions. The yields of H_2O_2 were practically identical in 1 M $NaNO_3$ saturated with hydrogen, nitrogen, or oxygen.

According to Bakh et al.[24], $G(O_2)$ increases with increase of $NaNO_3$ concentration while the change in $G(H_2O_2)$ is insignificant (Table 3).

In the radiolytic decomposition of 1 M $NaNO_3$ with Co^{60} γ-rays, Sharpatyi et al.[41] found that $G(O_2)$ was 0.4 molecule and fell to zero in the presence of 10^{-3} M glycerine.

Radiolysis of Nitric Acid

There are only a few published references to the radiolysis of aqueous nitric acid. Medvedovskii et al.[42] found that the integral dose corresponding to the setting up of a stationary potential in the Fe^{3+}/Fe^{2+} system was significantly smaller in nitric acid than in other acids at the same concentration. They think that this is related to the fact that NO_3^- is reduced by the action of radiation, and that HNO_2 is formed, which can easily oxidise Fe^{2+}.

Challenger and Masters[43] found that radiolytic reduction of Ce^{4+} in nitric acid gave a larger $G(Ce^{3+})$ than reduction in 0.8 *N* H_2SO_4; in 1 *N* HNO_3 $G(Ce^{3+})$ was 8.3 ions. According to their explanation, the increase is due to the formation of an additional quantity of reducing agent (HNO_2) by the reaction of OH radicals with HNO_3.

Zaitsev et al.[44] studied the reduction of Am^{6+} and Am^{5+} by their own α-particles in H_2SO_4, HNO_3, and $HClO_4$ (see Table 4).

It can be seen from Table 4 that the yield of AmO_2^{2+} in nitric acid is 1.5–2 times as large as the maximum yield from 0.2 M $HClO_4$ and 0.1 M H_2SO_4. They consider that reduction in nitric acid solutions occurs at the expense of the secondary products of the reaction between radicals and HNO_3.

Mechanism of Reduction of NO_3^- Ions

The available experimental data on the effect of ionising radiation on aqueous nitrate solutions is interpreted in different ways by various authors.. This is particularly true of concentrated solutions where the solute is subjected to the combined direct and indirect effects of the radiation.

It is generally accepted[23–25,28,29,45] that reduction takes place at the expense of H atoms formed during the radiolysis of water. In Bakh's opinion[23] the first stage in the reduction of nitrate to nitrite is reaction (34). The subsequent transition from NO_2 to NO_2^- can occur either by a second reaction with an H atom

$$NO_2 + H \rightarrow NO_2^- + H^+ \quad (39)$$

or, more probably, by disproportionation:

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3. \quad (40)$$

In both cases two H atoms are used up in forming a single NO_2^- ion.

Sharpatyi et al.[26,35] suggest that the reduction of nitrate by H atoms takes place by a somewhat different mechanism. Atomic hydrogen reacting with NO_3^- gives HNO_3^- or NO_3^{2-} ions (depending on pH), where the nitrogen is quadrivalent:

$$NO_3^- + H \rightarrow HNO_3^- \quad (41)$$

or

$$NO_3^- + H + OH^- \rightarrow NO_3^{2-} + H_2O. \quad (42)$$

Further, these ions can disproportionate or be oxidised to nitrate, thus:

$$2HNO_3^- \rightarrow NO_3^- + NO_2^- + H_2O, \quad (43)$$

$$HNO_3^- + O_2 \rightarrow NO_3^- + HO_2 \quad (44)$$

or

$$NO_3^{2-} + O_2 \rightarrow NO_3^- + O_2^-. \quad (45)$$

The authors believe that the decrease in $G(NO_2^-)$ in a nitrate solution saturated with air, compared with a solution saturated with nitrogen, confirms this mechanism.

It is also confirmed indirectly by the dependence of $G(NO_2^-)$ in 1 M alkaline $NaNO_3$ on the dose rate[36]. In solutions saturated with air, $G(NO_2^-)$ remains constant with change of dose rate between 2×10^{12} and 5×10^{16} eV $ml^{-1}sec^{-1}$. In the absence of oxygen (solution saturated with nitrogen) $G(NO_2^-)$ is independent of the dose rate between $\sim 2.5 \times 10^{13}$ and 5×10^{16} eV $ml^{-1}sec^{-1}$, but with a mixture of 2.5% oxygen and nitrogen $G(NO_2^-)$ is directly proportional to the logarithm of the dose rate. This is explained[36] by the simultaneous occurrence of disproportionation of the HNO_3^- ion and its oxidation to NO_3^- by oxygen.

Sharpatyi and Molin's[46] investigation of electron-paramagnetic-resonance (e.p.r.) spectra and kinetics of the build-up of radicals during radiolysis of a frozen aqueous sodium nitrate solution showed that NO_2 was the main product of the conversion of NO_3^- to NO_2^- and NO_2^- to NO_3^-. During the reduction of nitrate to nitrite a radical containing quadrivalent nitrogen (HNO_3^-) was also observed. These radicals only disappear at temperatures between -70° and -90°. The e.p.r. spectra showed that the yield of radicals from the reduction of nitrate ions depends on solution concentration and not on the nature of the gas saturating it, and increases with the addition of alkali or glycerine.

Thus the reduction of NO_3^- ions proceeds mainly by the action of atomic hydrogen formed by radiolysis of water. But $G(NO_2^-)$ in nitrate solution, with a concentration as low as 0.1 M, was found to exceed the value estimated on the assumption that all the H atoms are used up in reducing NO_3^- ions (1.8 to 1.9 ions for light-particle radiation and ~ 0.6 ion for α-particles). Some authors[28,29,45,47] explain the increase in $G(NO_2^-)$ in concentrated nitrate solutions as a direct effect of radiation on the solute. Sworski[45] found that the presence of nitrate in a solution of Ce^{4+} in 0.8N H_2SO_4 treated with Co^{60} γ-rays increased $G(Ce^{3+})$; the increase was the same in the presence and absence of Tl^+ ions (Fig. 2). Since Tl^+ is an effective acceptor of OH radicals, the observed increase in $G(Ce^{3+})$ in the presence of NO_3^- cannot be ascribed to the reaction between Ce^{4+} and these radicals. Sworski explains these results by the direct action of the radiation on the nitrate, consisting in excitation of NO_3^- ions on collision with low-energy electrons* or with excited water molecules.

Mahlman and Schweitzer[47] studied the action of Co^{60} γ-rays on solutions of a series of nitrates at concentrations from 0.001 M to 5.0 M and containing 2×10^{-4} M Ce^{4+} in 0.4 M H_2SO_4 (Table 5). The increase in $G(Ce^{3+})$ in sufficiently concentrated solutions (above 0.04 M) is connected with the formation of NO_2^- ions, which react with Ce^{4+}:

$$NO_2^- + 2Ce^{4+} + H_2O \rightarrow 2Ce^{3+} + 2H^+ + NO_3^-. \quad (46)$$

Since the increase does not occur in strongly acid dilute nitrate solutions, the effect observed in concentrated solutions is thought to result from the direct action of γ-rays on NO_3^- ions:

$$NO_3^- \sim\sim\rightarrow NO_2^- + \tfrac{1}{2}O_2. \quad (47)$$

It may be seen from Table 5 that the nitrite yield due to direct action, $G(NO_2^-)_{dir}$, does not depend on the nature of the cation. The dependence of $G(NO_2^-)_{dir}$ on NO_3^- concentration is expressed by the equation

$$G(NO_2^-)_{dir} = 1.22 \log [NO_3^-] + 1.70. \quad (48)$$

Kabakchi et al.[28,29] treated nitrate solutions between 0.1 M and near saturation with Co^{60} γ-rays, Pu^{239} α-particles, and P^{32} β-rays. Griess' reagent was added to the solutions to react with the nitrite ions at the moment of formation and to protect them against the radiolysis products of

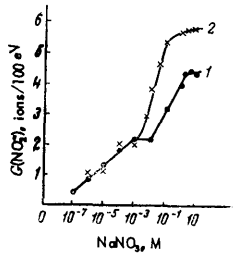


Fig. 4. Dependence of $G(NO_2^-)$ on the concentration of $NaNO_3$ (pH 14)[41]: 1) in absence of glycerine; 2) in presence of 10^{-3} M glycerine.

TABLE 5. Nitrite yield (ions /100 eV) through the direct action of Co^{60} γ-rays (from Mahlman and Schweitzer[47]).

NO_3^-, M	Cation									
	Li	Na	K	Rb	Cs	NH_4	Zn	Mg	Al	Th
0.1	0.54	0.50	—	0.48	0.52	0.55	0.49	0.53	—	0.50
0.14	—	—	0.68	—	—	—	—	—	—	—
0.15	—	—	—	—	—	—	—	0.69	—	—
0.20	0.82	0.88	—	—	—	0.83	0.86	0.78	—	0.78
0.30	1.07	1.02	—	0.89	1.14	1.04	—	—	0.90	1.19
0.34	—	—	1.12	—	—	—	—	—	—	—
0.40	—	—	—	1.22	—	—	1.17	1.19	—	—
0.50	1.36	1.33	1.39	1.37	1.38	1.37	—	—	—	1.38
0.60	—	—	—	—	—	—	1.27	1.27	1.21	—
0.90	—	—	—	—	—	—	—	—	1.39	—
1.0	1.86	1.62	1.73	—	1.76	1.72	1.63	1.54	—	1.74
1.36	—	—	1.94	—	—	—	—	—	—	—
1.50	—	—	—	—	—	—	—	—	1.75	—
1.75	—	—	2.02	—	—	—	—	—	—	—
2.0	2.10	—	—	—	—	2.11	—	1.79	—	2.19
3.0	—	2.24	—	—	—	2.53	—	—	2.03	2.54
4.0	—	—	—	—	—	—	—	2.42	—	—
5.0	—	2.59	—	—	—	2.71	—	—	—	—

* Low energy-electrons are produced in the ionisation of water[48,49]; they lose their energy by inelastic collisions. If this energy falls below the lowest excitation energy of water, these electrons can have a greater cross-section for reaction with solutes than with water. The part played by low-energy electrons in radiation chemistry is obscure.

water. Fig. 3 shows the relationship between $G(NO_2^-)$ and KNO_3 concentration for Co^{60} γ-rays and Pu^{239} α-particles (curves *1* and *2*); curve *3* was calculated from

$$G'(NO_2^-) = G(NO_2^-) - G(H)/2, \quad (49)$$

where $G(NO_2^-)$ is the total nitrite yield and $G(H)/2$ is the NO_2^- yield due to reduction of NO_3^- by H atoms. The independence of $G'(NO_2^-)$ of the type of radiation and the considerable influence of NO_3^- concentration is ascribed to direct action of the radiation. For comparison, curve *4* shows Mahlman and Schweitzer's[47] data for the direct effect of Co^{60} γ-rays on aqueous KNO_3.

Other explanations of the increase of $G(NO_2^-)$ in concentrated nitrate solutions are offered by a number of authors[1-3,23,24,32,50]. They consider that the excitation of water molecules, as well as their ionisation, plays a part. It may be seen from Table 2 that on adding glucose or glycerine to an alkaline nitrate solution $G(NO_2^-)$ increases by a factor of 3 (5 to 6 ions; i.e. the radiolysis products of water are completely used up). According to Proskurnin et al.[1-3,32,50] this increase in $G(NO_2^-)$ is due to some of the water molecules acquiring sufficient energy for ionisation, but being in one "cell", the H atoms and OH radicals recombine, not having time to diffuse into the bulk of the solution and react with the solute. The presence of two acceptor radicals, capable of reacting with the two parts of the dissociating water molecule (in this case the NO_3^- ion is the acceptor of the H atom and the glucose or glycerine is the acceptor of the OH radical), and the simultaneous occurrence of two coupled oxidation-reduction reactions, enable greater use to be made of the absorbed energy by drawing on the energy of excitation of water.

Work by Sharpatyi et al.[41] on the effect of $NaNO_3$ concentration in alkaline solutions (between 10^{-7} M and 6 M) on radiolytic transformations (Fig. 4) is of interest in this connection.

With increase of concentration from 10^{-7} M to 5×10^{-4} M $G(NO_2^-)$ increases and remains constant at ~4.3 equiv. between 5×10^{-4} M and 10^{-2} M. In more concentrated solutions, $G(NO_2^-)$ increases linearly into log [$NaNO_3$]. Between 1 M and 6 M $G(NO_2^-)$ again remains constant (~g equiv.). The addition of 10^{-3} M glycerine does not change the shape of the curve (Fig. 4, curve *2*), although it diminishes its sloping portion. The sloping portion of curve *1* is explained by the practically complete reaction of H atoms with nitrate ions.

At present the experimental material available is still insufficient to decide between one or another mechanism of the radiolytic transformations of nitrate solutions. For example, if we accept the hypothesis of Proskurnin et al., it is difficult to explain the considerable increase in $G(NO_2^-)$ observed by Sworski at large nitrate concentrations, even in the presence of such effective acceptors of H atoms and OH radicals as Ce^{4+} and Tl^+ ions. On the other hand, if we take into account the contribution of the solute to the electron density, which is 0.05 for 1 M $NaNO_3$ and 0.11 for 2 M, we find that the effect of the direct action of radiation, even on very concentrated solutions, is only a few percent. Additional factual material is therefore necessary for the final solution of the question of radiochemical processes in concentrated nitrate solutions; for example, reliable data about the initial yield of molecular oxygen; the effect of dose rate over a wide range on the yield at different NO_3^- concentrations; the determination by electron paramagnetic resonance of the concentration and nature of the free radicals appearing immediately on irradiation; etc.

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PROGRESS IN THE ANALYTICAL CHEMISTRY OF URANIUM, THORIUM, AND PLUTONIUM

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INTRODUCTION

Extensive use of atomic energy had led to the rapid development of the analytical chemistry of uranium, thorium, and plutonium, and several thousand papers on this subject have been published.

Numerous data on the chemistry of uranium, thorium, and plutonium are collected in the monograph by Seaborg and Katz (Russian translation edited by Nikolaev[1]) and in a recent monograph by Seaborg[2]. The most complete review of the literature on the analytical chemistry of thorium is given in a monograph by Ryabchikov and Gol'braikh[3]. The analytical chemistry of uranium is dealt with in monographs and review articles by Rodden[4-6], Palei[7], and others[8-23]; interesting data on the chemistry of thorium are given in reviews by Rodden[4,24], Schoeller[25], Moeller[26], Bonardi[27], and others[8,11,31,28,29], and on the chemistry of plutonium in reviews by Metz and Harvey[30-34].

This article reviews modern chemical methods for determining uranium, thorium, and plutonium, and discusses the analytical reactions of these elements. Physical, physicochemical, and other instrumental methods, which

have been reviewed elsewhere[1,4,20,35-40], are dealt with in less detail.

The analytical chemistry of neptunium has been reviewed by Alimarin and Zolotov[41], but little has yet been published on the analytical chemistry of the other transuranic elements.

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A characteristic feature of the analytical reactions of uranium, thorium, and plutonium is the close similarity between ions of the same type, which results from the similarity in the electronic structures of the elements. The pH values at which hydrolysis of the cations of the elements begins are almost identical, which means that the conditions under which the corresponding analytical reactions take place are closely similar. Differences are shown in some specific reactions, e.g. the luminescence of uranyl compounds.

The reactions of the U^{4+}, Th^{4+}, and Pu^{4+} cations also resemble those of Zr^{4+}, Ti^{4+}, and Ce^{4+}. The pH values required for reactions related to the ease of hydrolysis of these cations lie in the same order as those of the "start of precipitation of the hydroxides": i.e. Ti^{4+} (< 2), Zr^{4+} (2), Pu^{4+} (3), U^{4+} (3.2), and Th^{4+} (4).[1] Reactions of this class include many colour reactions with organic reagents, precipitation reactions, etc.

Similarities are also shown by the UO_2^{2+} and PuO_2^{2+} ions, and by the Pu^{3+} and U^{3+} ions. Considerable differences are shown, however, by the redox reactions. Although thorium(III) is known, Th^{3+} ions in aqueous solution are so unstable that the redox reactions cannot be used for analytical purposes[1].

Uranium is most stable as the cation UO_2^{2+}. Uranium(IV) is oxidised in air as readily as, or even more readily than ferrous salts. Uranium(III) is a powerful reducing agent, and its salts are oxidised in air as readily as titanium(III) salts.

Plutonium(IV) is stable in air. Plutonium(III), unlike uranium(III), is not a powerful reducing agent, and Pu^{3+} salts are oxidised in air at approximately the same rate as uranium(IV) or ferrous salts. The PuO_2^{2+} ion is a weak oxidising agent, of approximately the same strength as elemental iodine.

The most important chemical methods for separating uranium, thorium, and plutonium from other elements depend on the variable oxidation state of plutonium and uranium and the ability of Pu(VI), Pu(IV), U(VI), U(IV), and Th nitrates to be extracted from aqueous solution by oxygen--containing organic solvents immiscible with water. Methods involving the precipitation of Pu(IV), U(IV), and Th from strongly acidic solution, and some chromatographic methods, are also fairly selective.

The chief chemical methods for the determination of the elements are: redox volumetric for U and Pu; volumetric complexometric for Th, Pu(IV) and U(IV); gravimetric for all three; and photometric for U(IV), U(VI), Pu(IV), and Th.

The colour reactions of the +4 cations are carried out in solutions acidified with inorganic acids, and in a number of cases this forms the basis for their direct determination in the presence of +1, +2, and +3 foreign cations whose colour reactions occur in less strongly acidic solutions.

1. REACTIONS OF URANIUM, THORIUM, AND PLUTONIUM IONS IN AQUEOUS SOLUTION

A. Reactions of Uranium

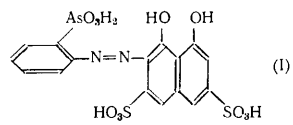
In acid solutions free from sulphate, phosphate, fluoride, and other complex-forming substances, uranium(VI) is present as solvated UO_2^{2+} ions, which give the solutions a yellow-green colour. When the pH is increased to ~4.5, the UO_2^{2+} ions are hydrolysed and converted to the soluble $UO_2(OH)^+$ cations[1,4], or, according to other data, to the polycations $U_2O_5^{2+}$ and $U_3O_8^{2+}$.[42,43] Subsequently, insoluble uranates $M_2U_2O_7$ or more complex salts are formed[44-47]. Some authors doubt the existence of UO_2^{2+} ions and consider that basic salts of $U(OH)_4^{2+}$ or $U^{6+}.2UO_3$ are formed[48-54].

At high concentrations of nitrate or chloride in acid solutions, uranyl ions form unstable complexes $UO_2NO_3^+$, $UO_2.(NO_3)_2$, UO_2Cl^+, UO_2Cl_2, $UO_2Cl_4^{2-}$, etc.[1,6]. The sulphato complexes are more stable, so that in solutions containing sulphate, many reactions of uranyl ions (colour reactions, some precipitation reactions, etc.) are not complete. Phosphato complexes are much more stable than the sulphato complexes, and in weakly acidic and neutral solutions, phosphate masks all the reactions of uranyl ions. Phosphato complexes are not formed in strongly acidic solutions[55].

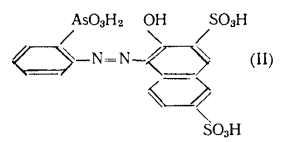
From pH 4–5 upwards, i.e. in the range where UO_2^{2+} cations start to undergo hydrolysis, uranium(VI) forms compounds with various organic ligands[56-59]. Tartaric, citric, and other hydroxycarboxylic acids form hydrophilic anions which are difficult to precipitate and cannot be extracted. These ligands suppress the reactions of UO_2^{2+}, except in strongly acidic media.

At pH 4–7, Trilon B (sodium ethylenediaminetetraacetate, versene, Complexone III, EDTA) and its analogues form comparatively weak complexes with UO_2^{2+}, but have a marked masking action on many other elements[60-69]; this distinguishing feature of uranium(VI) is widely used in analytical chemistry[70-78].

Uranium(IV) is present as solvated U^{4+} cations, in sufficiently acidic solutions, and these have a comparatively intense green colour. These cations are hydrolysed at pH 2.0–3.0, and react with organic reagents of general formula R–OH, such as arsenazo(I) and thoron(II) in more strongly acidic media than U(VI) [79], so that the reactions of U^{4+} are more selective than those of UO_2^{2+}:



(I)



(II)

Nitrato, chloro, sulphato, phosphato, and fluoro complexes of U(IV) are much more stable than those of U(VI).[79-81] The nitrato, chloro, and sulphato complexes exist in both strongly acidic and weakly acidic solutions, but the phosphato and fluoro complexes only in weakly acidic solutions. Chlorides and nitrates do not mask the colour reactions of U^{4+}, but sulphates, and more particularly, phosphates and fluorides, have a strong masking action. The complexes of U(IV) with organic ligands are similar to the correspond-

ing U(VI) complexes. Unlike uranium(VI), uranium(IV) forms stable complexes with Trilon B.

The reactions and conditions for the existence of uranium(IV) ions resemble those of thorium ions.

In acidic and neutral solutions, uranium(III) is present as solvated U^{3+} cations, whose red-violet solutions are rapidly oxidised by atmospheric oxygen, so that reactions involving oxidation of U^{3+} are difficult to study in open vessels.. Complex U(III) ions appear to be analogous to the corresponding complexes of the rare-earth elements.

Uranium(V) exist in solution as UO_2^{2+} ions, which are fairly stable only at pH 2–4.[1,50,82] Uranium(V) disproportionates to U^{4+} and UO_2^{2+} ions with change in the pH or on prolonged standing. The analytical reactions of U(V) have been little studied.

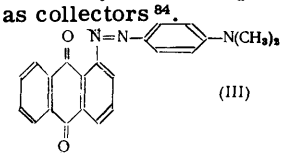
The precipitation reactions of the various uranium ions are not the same. The best known are the precipitation reactions of UO_2^{2+} ions, which form sparingly soluble uranyl salts or hydrolysis products. Most precipitants which have been described contain oxygen and react with uranyl ions to form a U(VI)–O bond, so that they are effective only at those pH values at which this bond can exist, i.e. at pH 4–5 and above. Precipitation by oxygen-containing inorganic (NaOH, NH_4OH, Na_2HPO_4, etc.) and organic (8-hydroxyquinoline, quinaldinic acid) precipitants is not selective, and the same is true of sulphur-containing reagents.

Potassium ferrocyanide precipitates uranyl ions from solutions which are not too strongly acidic[82], and since the precipitate has a bright reddish-brown colour the reaction is usually employed not as a precipitation reaction but as a colour reaction for uranium.

Methods for the precipitation of uranium(IV) are more selective. The precipitation is carried out from fairly strongly acidic solutions, so that elements present as ions which are difficult to hydrolyse remain in solution. Uranium(IV) appears to be precipitated by all precipitants used for thorium and zirconium, although not all such reactions are described in the literature. The ease of oxidation of uranium(IV) salts makes their analysis difficult, but this can be overcome if the precipitation is carried out from solutions containing a powerful reducing agent.

Precipitation of U(IV) by ammonia or alkalis in the absence of reducing agents is not specific, since U(IV) is oxidised very rapidly in alkaline solutions. Phosphate precipitates U(IV) in inorganic-acid solution, and this is used to coprecipitate uranium phosphate with thorium or zirconium phosphate, with subsequent oxidimetric determination of the U(IV) (Volkov's method)[7].

Like the cations of thorium and other elements in oxidation state IV, U(IV) ions are precipitated by many organic anions of high ionic weight; a characteristic example is the precipitation by various arylarsonic acids $Ar-AsO_3H_2$.[83] Uranium(IV) should be precipitated from strongly acidic solutions in the form of complex anions such as UCl_6^{2-} and similar ions, but such reactions have not been described. Uranium(VI) in the form of its anionic thiocyanato complex can be precipitated from extremely dilute solutions (0.1–1 γ/litre) with the heavy organic cations of anthrazo(III) or methyl violet, whose thiocyanates are precipitated simultaneously and act as collectors[84].



(III)

Some theoretical problems related to the coprecipitation of elements with organic collectors have been discussed by Kuznetsov[85,86].

The extraction of uranium may be carried out in a number of ways: by "physical distribution" of uranyl nitrate between aqueous and non-aqueous phases, as oxonium salts from strongly acidic solutions, and as the hydrophobic complexes formed by uranyl ions with various organic compounds[87–101].

The extraction of uranium in the form of its nitrato compounds is of great practical importance. Uranyl nitrate can be extracted from aqueous solutions by many oxygen-containing organic solvents immiscible with water, the most efficient of which are compounds containing carbonyl oxygen, and esters containing one oxygen atom per 4–7 carbon atoms. Ethers are much less efficient. The compounds extracted are complexes of general formula $UO_2(NO_3)_2 . mH_2O . nS$, where S is the solvent, m = 2–4, and n most frequently equals 2. The presence of the two water molecules possibly indicates the existence of $U(OH)_4^{2+}$ (= $UO_2 . 2H_2O^{2+}$).[48]

Fairly efficient extraction is usually achieved from solutions with high concentrations of nitrates, which act as "salting-out agents", and in the absence of complex-forming masking agents capable of combining with uranium to form hydrophilic complexes which are not extracted[88]. The most efficient salting-out agents are nitrates which crystallise with water of crystallisation, i.e. those of aluminium, iron, zinc, and calcium. Ammonium and alkali-metal nitrates, which crystallise without water of crystallisation, are less efficient[88]. The salting-out activity of a number of substances has been compared by Vdovenko and others[102–106].

Extraction is possible from weakly acidic solutions and also from concentrated nitric-acid solutions[107]; in the latter case the extraction proceeds even in the presence of phosphate and other complex-forming substances, which do not combine with uranium under these conditions. Certain experimental data indicate that uranium is extracted from strongly acidic solutions not only in the form of nitrato compounds, but also as salts of complex nitratouranate anions and oxonium cations formed by solvent molecules with hydrogen ions[88,108]. The extraction of uranium in the form of its nitrato compounds is the best method for separating uranium from other elements, since the only other metals extracted are thorium, plutonium, and, to some extent, scandium and gold. Other elements are extracted to a very small extent[88].

The extraction of uranium as the thiocyanate is complete, but is less selective than the extraction of nitrato compounds[109]. Uranium can also be extracted from hydrochloric-acid solutions in the form of salts of chlorouranate anions and heavy hydrophobic organic cations such as the tribenzylammonium cation[88,100]. Many elements form complex chloro anions in hydrochloric-acid solution so this method is less selective than extraction of nitrato compounds.

Like many other elements, uranium is extracted in the form of the salts formed with a number of organic precipitants, whose molecules do not contain the hydrophilic SO_3H, COOH, or NH_2 groups. Extraction is possible at pH values at which the salts exist, i.e. pH 3.5 and above, and this method can be used not only with oxygen-containing organic solvents, but also with others such as chloroform[111–116]. This type of extraction, like the corresponding precipitation reactions, is not selective.

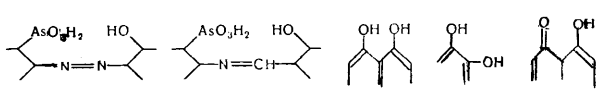
Many workers have developed interesting methods of extraction in the presence of Trilon B, which greatly increases the selectivity of the separation of uranium [109].

Like uranium(VI), uranium(IV) is extracted both as the nitrate and as the chelate compounds formed with the organic reagents 8-hydroxyquinoline, cupferron, and many others. These compounds are formed in more strongly acidic solutions in the case of U(IV) than in the case of U(VI), so that the extraction of the former is more selective, and U(IV) and U(VI) can be separated at low pH values. The advantages of extraction methods for the separation of uranium are the high selectivity, speed, and convenience, and the possibility of working with very small quantities of the element. The thermodynamics of the extraction equilibria for uranyl nitrate have been discussed by Rozen [87]. Various other theoretical problems related to the extraction of elements have been examined by Irving, Nikolaev, and others [88-90,117-119].

The normal redox potential of the U^{4+}/UO_2^{2+} system is -0.32 V, [1,120,121] but UO_2^{2+} ions are reduced rapidly only by very powerful reducing agents, and not by weak reducing agents which might have been expected to do so from their redox potentials. This may be due either to the fact that in actual solutions uranium is not likely to be present as non-hydrated uranyl cations, or to the slow rate of the processes taking place. Slow rates of reduction are characteristic of uranyl ions. In photochemical reactions, uranyl ions are reduced even by such weak reducing agents as ethyl alcohol or diethyl ether, but the reduction is again slow. Uranium(IV) is rapidly oxidised, however, even by weak oxidising agents, and this is used for the volumetric determination of uranium. A number of theoretical problems related to redox methods for determining uranium have been discussed by various authors [1,122,123].

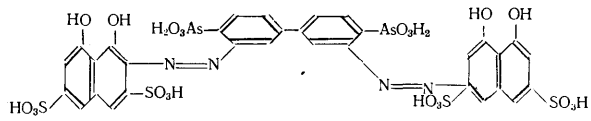
General colour reactions based on the reducing action of U(IV) and U(III) may exist, but none have been described.

Colour reactions for uranium are of two main types, the first based on the chromophoric action of U–O and U–S groups [124-127], produced by interaction between uranium and the colourless or weakly coloured reagents hydrogen peroxide, salicylic acid, nitroso-R salt, thiocyanate, and alkyldithiocarbamates. The formation of coloured simple inorganic compounds, such as perchlorates, phosphates, and others, is also used, but these methods, particularly for U(VI), are not sensitive. In all cases, U(VI) gives a yellow or brown colour, while U(IV) gives green colours. Colour reactions of the second type involve the formation of complexes by uranyl ions and coloured reagents containing various atomic groupings capable of combining with uranium, such as



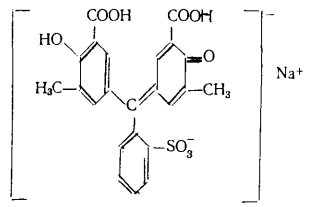
and others [128]. The changes which take place in the reagent molecules as a result of complex-formation lead to a marked deepening of the colour. The mechanism of colour reactions of this type has been discussed [128-147].

Since the colour of the uranyl ion is produced only at intermediate pH values, not less than 4–5, at which other elements also react with these groupings, the selectivity of the reactions is not high. The colour reactions of uranium(IV) take place in more strongly acidic solution and are more selective. The sensitivity of reactions of this type is very high. Interesting reagents of this type include arsenazo I, mentioned above, arsenazo II(IV):



(IV)

quinizarinsulphonic acid, and Eriochrome Cyanine R(V):



(V)

A solid-phase colour reaction [148] has been described for the chlorouranate(VI) anion with anthrazo reagent [149]. Since the complex anion is stable only at high acidity, the reaction is carried out in 6–12 *N* HCl.

The chromophoric action of the uranium(IV) grouping U(IV)...O is less marked than that of U(VI)...O, so that the corresponding colour reactions of U(IV) with colourless inorganic or organic reagents are more sensitive, can be carried out at lower pH values (1–4), and are therefore more selective.

The colour reactions of uranium(IV) with coloured organic reagents are also of interest. They are slightly less sensitive than the corresponding reactions of uranyl ions, but are carried out in much more strongly acidic solutions and are much more selective. Colour reactions of this type for U(IV) resemble those for Th and are carried out under approximately the same conditions with the same reagents, particularly arsenazo and thoron [7,150,151].

Sensitivity and selectivity of the analytical reactions of uranium. Values of the "gamma sensitivity indices" for some reactions of uranium are given in the Table.

Gamma sensitivity index* for some reactions of uranium(VI).

Reagent	Reaction conditions			Gamma sensitivity index
	pH	reagent concentration, M	wavelength, mμ	
Arsenazo	6.0	0.00003	572	0,083
Potassium ferrocyanide	5.0	0.008	458	0,017
Sulphosalicylic acid	9.5	0.08	458	0,003
$H_2O_2 + Na_2CO_3$	9.5	0.018	458	0,0014
Actual colour of uranyl salts	1.8	—	413	0,000025

* The gamma sensitivity index is the difference between the light absorption of the reaction product and that of the same quantity of reagent as is combined in the reaction product. The difference is related to a solution with an element concentration equal to 1 γ/ml and a layer thickness of 10 mm. [152]

The most sensitive and selective reaction is the fluorescent reaction in fused NaF, which permits the determination of 0.001 γ of uranium. The next most sensitive reaction is that with arsenazo, which permits the determination of 0.1 γ of uranium per ml, but which has a low selectivity. Potassium ferricyanide permits the determination of 0.5 γ/ml and sulphosalicylic acid and other organic reagents 1–2 γ/ml.[7]

The spectral method can be used for specimens containing 0.005% uranium, the polarographic method for concentrations of 10^{-3}–10^{-5}% uranium, and oscillographic polarography for concentrations of about 10^{-6}%.[20]

The low stability of UO_2^{2+}–Trilon B complexes and the ability of organic solvents to extract uranyl nitrate are used in various combinations to achieve high selectivity in the determination of uranium[7,153], particularly by the sensitive, but insufficiently selective, reaction with arsenazo[147]. The reactions of tetravalent uranium are much more selective.

B. Reactions of Thorium

Thorium does not form chromophoric atomic groupings and shows an almost invariable oxidation state, so that the element has fewer analytical reactions than uranium or plutonium. No direct redox reactions are known, and colour reactions are possible only with coloured organic reagents[128,129].

In acid solutions thorium forms solvated Th^{4+} cations which undergo stepwise hydrolysis, from pH 2–3 upwards, to form complex solvated +3, +2, and +1 cations. The degree of hydrolysis depends on the pH, thorium concentration, solution composition, and other factors. When the solutions are acidified, the hydrolysed thorium ions are readily reconverted to the reactive Th^{4+} ions. This ready breakdown of the polynuclear ions or oxoions differs from the behaviour of Zr, Ti, and other heavy metals, but resembles the behaviour of uranium, and is particularly favourable for colour reactions.

Thorium ions have a marked tendency to form complexes,, and in the presence of large quantities of nitrate and chloride they form the complex anions $Th(NO_3)_6^{2-}$ and $ThCl_6^{2-}$, which exist in strongly acidic solutions[110]. Both anions are unstable, so that the presence of nitrate or chloride does not interfere with the usual reactions of Th^{4+}. Sulphate, and more particularly fluoride and phosphate, however, form fairly stable complexes with thorium and mask its reactions so completely that a method for the determination of fluorides[154], and extremely sensitive colour reactions for sulphate and phosphate[155], have been based on this property.

In weakly acidic or neutral solutions, Trilon B, oxalic acid, many hydroxycarboxylic acids, and other organic complex-forming substances form stable complexes with thorium[156]. Direct analytical reactions of the colourless hydrophilic anions formed by thorium with these substances have not yet been described.

Precipitation reactions. At approximately the same pH values at which hydrolysis starts (pH 2.5–4) thorium cations are precipitated by many organic reagents which form chelate compounds containing the Th–O bond. These methods can be used to separate thorium from the rare-earth and many other elements which are precipitated only in less strongly acidic solutions.

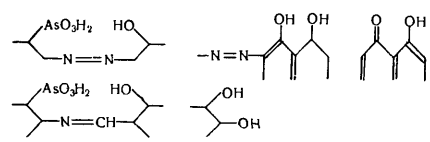
Thorium cations can also be precipitated from strongly acidic solutions as normal salts with various inorganic and heavy hydrophobic organic anions. Thorium forms a sparingly soluble fluoride, phosphate, iodate, molybdate, and tungstate. Organic precipitants include oxalic acid and various monobasic acids with molecular weights greater than 150–200. Arsonic, seleninic, and sulphinic acids are efficient and fairly selective precipitants.

Extraction methods. Although thorium nitrate, $Th(NO_3)_4 \cdot 4H_2O$, dissolves in many organic oxygen- and nitrogen-containing solvents, it can be extracted by only a few of these, and then only in the presence of salting-out agents. It is readily extracted by compounds with carbonyl oxygen — ketones and esters — and less readily by ethers[157–160]. Various metal nitrates are used as salting-out agents, and their efficiency is approximately the same as in the extraction of uranyl nitrate[88,105]. Tributyl phosphate extracts thorium nitrate efficiently without a salting-out agent[3,4].

Mesityl oxide, which is most frequently recommended for the extraction of thorium nitrate, permits separation from the rare-earth and many other elements. Extraction is possible from weakly acidic solutions in the presence of salting-out agents and also from solutions in concentrated HNO_3;[88] in the latter case most of inorganic and organic complex-forming substances do not interfere. Sulphates appear to prevent the extraction of thorium, even from strongly acidic solutions. Thorium is extracted from solutions in concentrated acids to a considerable extent by an oxonium mechanism in the form of a salt of the complex anion, such as $Th(NO_3)_6^{2-}$, and an appropriate oxonium cation[88].

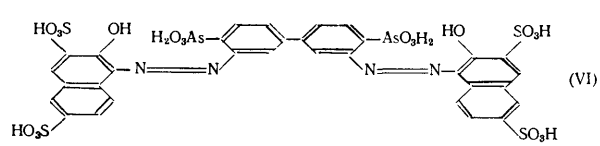
Thorium can be extracted according to general rules as the chelate and simple salts formed by organic complex-forming substances with a heavy hydrophilic molecule[88]. Extraction is possible in the absence of masking agents, at the pH values at which these salts exist. The separation is made selective by keeping the pH as low as possible. Extraction methods appear to be the most selective for the separation of thorium from other elements, and separation from zirconium, titanium, and the rare-earth elements can be achieved in one operation.

Colour reactions. A large number of these have been described. The great majority of reagents used are azo dyes — intensely coloured substances which can act as pH indicators[128–131]. A necessary condition for a colour reaction is the presence of a complex-forming atomic grouping characteristic for thorium, such as



etc.

The most interesting reagents are those containing the arsono group: arsenazo I, arsenazo II, thoron I, and thoron II(VI):[147]



(VI)

These and other reagents containing sulphonate groups form soluble compounds with thorium, but in the presence

of excess thorium suspensions may be formed which appear to consist of simple salts of thorium and a complex anion formed by thorium with the reagents. These suspensions dissolve when sufficient reagent is added.

The colour reactions of thorium with thoron II can be carried out in 4–6 *N* HCl[147], with arsenazo II and thoron I in 0.1–0.5 *N* HCl, and with others at pH above 1.5–2.[136] Since other elements (except Zr, Ti, and Hf) do not give colour reactions with the reagents at such high acidity, the selectivity of the determination of thorium is high. Masking agents such as sulphate, fluoride, phosphate, organic hydroxyacids, etc., interfere with the colour reactions of thorium and as a rule should be removed before the determination.

Arsenazo II and thoron II form very stable complexes with thorium, so that the element can be determined directly in solutions containing large quantities of sulphate, phosphate, and other compounds[147].

The most sensitive reactions for thorium appear to be the luminescent reaction with morin and the colour reaction with aminothoron, which permit the determination of 0.003 γ/ml and 0.1 γ/ml Th respectively. No photometric method for the determination of thorium has been described, but a qualitative test has been reported[147]. Arsenazo and thoron permit the determination of 0.2 γ/ml and 0.5 γ/ml Th respectively. Volumetric methods involving titration with Trilon B, fluoride, and oxalate are suitable for the determination of 0.2–20 mg of thorium.

The selectivity of methods for determining thorium is satisfactory, that of the photometric determination with coloured organic reagents being very high. The selectivity of other methods can be increased by preliminary extraction of thorium nitrate. The precipitation of thorium as the oxalate is fairly selective, and precipitation as the iodate slightly less so. In the presence of complex-forming compounds, thorium is selectively precipitated by phytic acid, a derivative of pyrophosphoric acid[162].

C. Reactions of Plutonium

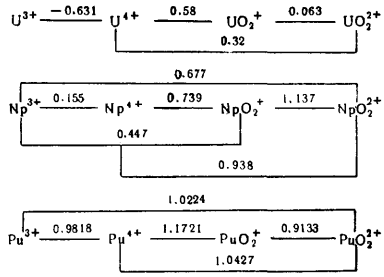
Plutonium exhibits several oxidation states and readily forms various complex ions and chromophoric atomic groupings, so that the analytical chemistry of plutonium is as varied and complex as that of uranium, although comparatively little has been published. Because of the high specific activity of all plutonium isotopes (Pu^{242}, Pu^{240}, Pu^{239}, Pu^{238}, Pu^{236}, etc.), radiometric methods are the most important.

Plutonium ions exist in aqueous solution in oxidation states III, IV, V, and VI, the most stable being the IV state. Many of the properties of Pu^{4+} ions, except the redox properties, are intermediate between the corresponding properties of thorium and zirconium. Like thorium, Pu(IV) has a marked tendency to form complexes. In the presence of nitrate, Pu(IV) forms the extremely characteristic complex nitrato anions, $Pu(NO_3)_6^{2-}$, and possibly other species, including the neutral nitrate[163]. In nitrate solutions with concentrations > 1 M or in 1–4 M HNO_3, almost all the Pu(IV) is present as undissociated $Pu(NO_3)_4$. At higher HNO_3 concentrations, part of the Pu(IV) forms anions of $HPu(NO_3)_5$ and $H_2Pu(NO_3)_6$: in 11 M HNO_3, anions of $H_2Pu(NO_3)_6$ alone are formed[164]. Nitrato complexes of Pu(IV) are fairly stable and for this reason nitric-acid solutions of plutonium have a different colour from its hydrochloric- or perchloric-acid solutions[163].

At high hydrochloric-acid concentrations Pu(IV) forms the complex anion $PuCl_6^{2-}$.[1] In less strongly acidic solutions, from pH 2.5–3.5 upwards, Pu(IV) forms soluble coloured carbonato compounds[165,166], and also oxalato[167,168], tartrato, citrato, ethylenediaminetetraacetato, and other complexes[1,169].

Oxidising agents of intermediate strength, such as elemental bromine, slowly oxidise Pu(IV) to Pu(VI), but oxidation by powerful oxidising agents such as Ce(IV) or MnO_4^- is more rapid. Powerful reducing agents, and hydrogen in the presence of platinum, rapidly reduce Pu(IV) to Pu(III).[1]

The normal redox potentials of systems formed by various oxidation states of Pu, U, and Np are given below*:



When hydrochloric- or nitric-acid solutions of plutonium, free from complex-forming substances, are evaporated to dryness on a water bath with several drops of HBr and then with HNO_3, all other oxidation states are converted to Pu(IV).

Plutonium(VI) forms ions analogous in composition and properties to those of uranium(VI). The colour of PuO_2^{2+} salt solutions varies between yellow and orange-pink[2], but plutonyl nitrate solutions have a greenish colour. Reducing agents such as iodide ions slowly reduce plutonium to the +4 state. Plutonyl-salt solutions are quite stable in air.

Plutonium(III) exists in aqueous solutions as Pu^{3+} ions, which are comparatively stable in air and whose chemical properties resemble those of the rare-earth elements. The colour of the solutions varies between blue and violet[2].

Plutonium(V) exists in aqueous solutions as PuO_2^+ ions. Solutions of Pu(V) in 0.2 M HNO_3 are obtained by the reaction Pu(III) + Pu(VI) $\rightleftharpoons$ Pu(IV) + Pu(V) when solutions of Pu(III) and Pu(VI) are mixed. The reaction is rapid when the mixture is shaken with a solution of tributyl phosphate in benzene to extract the Pu(IV). Pure Pu(V) remains in the aqueous phase, but gradually disproportionates to form Pu(IV) and Pu(VI) ions[1,170–173]. The chemical properties of Pu(V) have been insufficiently studied.

The sensitivity and selectivity of the analytical reactions of plutonium. Radiometric methods using commercial α-counters permit the determination of 0.001–0.01 γ of plutonium. The reactions with arsenazo or thoron permit the determination of 0.1–0.5 γ/ml Pu. Analysis of the peaks in the absorption spectra of plutonium-salt solutions is convenient for the determination of the various oxidation states of plutonium in their mixtures[1,174,175]. Several milligrams of plutonium are required for the determination.

* These values refer to 1 M perchloric-acid solutions (Ed. of Translation).

A feature which distinguishes Pu(IV) from many elements and from other oxidation states of plutonium itself is its ability to form the fairly stable complex anion $Pu(NO_3)_6^{2-}$. The precipitation of Pu(IV) in the form of salts of this anion is extremely selective. Extraction with ketones is fairly selective: Pu(IV) nitrate is readily extracted while Pu(III) is not. If plutonium is present as Pu(III), U(IV) and Th can be separated by extraction, and after conversion of the Pu(III) to Pu(IV), the latter can readily be separated from all other elements. Other schemes for the selective extraction of plutonium are possible.

2. METHODS FOR THE SEPARATION OF URANIUM, THORIUM, AND PLUTONIUM FROM OTHER ELEMENTS

A. Methods for the Separation of Uranium

Precipitation. Separation methods based on the precipitation of uranium(VI) are not very selective. Hydrolytic precipitation of uranium with ammonia [75,176-178], pyridine, urotropine [179-182], ethylenediamine [183], ammonium benzoate [184,185], and tannin [186-189] achieve separation only from the alkali metals and a number of divalent metals including the alkaline-earth metals, and also give partial separation from the rare-earth elements. The selectivity is not greatly increased by using reagents which precipitate uranium in the form of chelate compounds: cupferron [190-193], 8-hydroxyquinoline [75,194,195], quinaldinic acid [196], α-nitroso-β-naphthol [197,198], arsanilic acid [199], cacodylic acid [200,201], and others [202-208].

The precipitation of uranium as peroxouranic acid $UO_4 \cdot 2H_2O$ with hydrogen peroxide is slightly more selective [4,209,210] and achieves separation from Ag, Al, Zn, and the alkaline-earth elements. Slight coprecipitation of Cu and Pb, and marked coprecipitation of Fe, P, and Si, take place [209]. The precipitation is carried out using 0.01–0.2 M uranium solution and a slight excess of H_2O_2 at pH 2–2.5 and 40–50°. [209,210] According to other data, the solution should be cooled and filtered at 2°. [4] In alkaline medium, H_2O_2 reacts with uranyl ions to form a stable soluble complex which is not broken down by ethylenediaminetetraacetic acid, and this is used in the complexometric determination of the alkaline-earth metals in the presence of uranium [211].

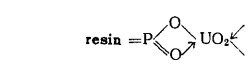
A characteristic and in most cases efficient method of purification uses sodium carbonate with which uranium forms a soluble carbonato complex, $Na_4[UO_2(CO_3)_3]$, while many other elements are precipitated as hydroxides or carbonates [4,7,212,213].

The precipitation of U(VI) by oxoacids of phosphorus [214-219], arsenious acid, potassium ferricyanide, ammonium vanadate, and other precipitants [220-227] is not selective and permits separation only from the alkaline-earth, rare-earth, and a few other elements.

The selectivity of the precipitation of uranium from solutions containing Trilon B is much higher. Methods have been described for precipitation with ammonia [70,75], cupferron [76], 8-hydroxyquinoline [71,73,75,78], and ammonium phosphate [74,216,225], and for electrolytic deposition [226]. Complete separation is achieved from Fe, Cr, Cu, Ni, V, Ce, Bi, and many other elements.

Uranium(IV) may be precipitated using phosphate, fluoride, or cupferron [227,228]. Small quantities are readily coprecipitated with $BaSO_4$, and uranium(VI) and thorium are not coprecipitated [229]. Uranium may be coprecipitated from extremely dilute solutions with Al and Fe hydroxides or phosphates [218 230], with double sulphates of the rare-earth elements [231], or with organic coprecipitants. Kuznetsov and Akimova have developed a method for the coprecipitation of uranium from sea water with the insoluble methyl violet thiocyanate. The limiting dilution of uranium is $1:10^{10}$ (0.1 γ/litre U). The uranium is determined fluorimetrically after separation [84].

Chromatographic methods. Ion exchange is widely used for the technical and analytical separation of uranium. A distinguishing feature of these methods is that even extremely small amounts of uranium may be separated completely from large amounts of impurities [232-254]. The use of complex-forming resins containing phosphinic-acid groups for the separation of very small quantities of uranium from heavy metals is of particular interest. It is reported that complexes of the type



are 10^6 times more stable than the corresponding monomers [254]. Partition chromatography using columns of cellulose [225-258] or silica gel [76] is, in effect, continuous extraction. Paper chromatography is used for work with small amounts of material [259-266]. General problems related to the chromatographic separation of elements have been discussed in reviews by Ryabchikov, Senyavin, and others [232-237].

Extraction methods for the separation of uranium as nitrato compounds are well known. Diethyl ether is most frequently recommended as extracting agent [111,267-274], rather unjustifiably, since the uranium distribution constant for this solvent is small compared with that for other solvents [88], and the inflammability of ether makes its use dangerous. More convenient extracting agents include ethyl acetate [218,275-286], mixtures of tributyl phosphate with other solvents [120,287-295], methyl isobutyl ketone ("hexone") [116,296,297], and many other oxygen-containing solvents [298-302]. After extraction of uranyl nitrate with tributyl phosphate, the uranium can be re-extracted by washing with 5–10% solutions of $(NH_4)_2CO_3$, Na_2CO_3, $H_2C_2O_4$, $(NH_4)_2SO_4$, or CH_3COONH_4. [295]. It is reported that solutions of the organophosphorus compounds $(RO)_3PO$, $(RO)_2RPO$, $(RO)R_2PO$, and R_3PO in CCl_4 are efficient extracting agents for uranium and plutonium [303].

Nitrates of ammonia [273], sodium [304], aluminium [276-280,285], iron, and other elements [102-106] are used as salting-out agents. Extraction from concentrated nitric acid [291] and extraction using triisooctylamine [312] have been much recommended.

A variety of reagents are used for the extraction of uranium in the form of hydrophobic chelate compounds, including cupferron [111,114,228,305], 8-hydroxyquinoline [113,116,306], dibenzoylmethane [307,308], acetylacetone [309-311] dibutyl hydrogen phosphate [207], and sodium diethyldithiocarbamate [112,115,313,314]. Uranium is readily extracted from carbonate solutions as the 8-hydroxyquinolinate by methyl isobutyl ketone [315], and the same solvent also extracts the diethyldithiocarbamate. Methods have been described for the separation of U^{233} from Bi^{212} and Pb^{212}. [300]

Uranium is extracted as anilinium triacetatodioxouranate $C_6H_5NH_3[UO_2(CH_3COO)_3]$ by alcohols and ketones [316]. Apparatus used for the extraction of uranium and other elements is described in monographs by Morrison and Freiser [317], and others [318-320].

B. Methods for the Separation of Thorium

Precipitation. Thorium can be separated from the alkali, alkaline-earth and rare-earth metals, Mn, Ni, Co, Cu, Zn, Cd, and other elements by precipitation with ammonia, pyridine, urotropine, or ammonium thiosulphate [321-328], and from Zr, Nb, Ta, and Sn by precipitation with fluoride [329-332].

The classical oxalate method permits separation of thorium from most elements except Ca, Sr, Ba, and the rare-earth elements [333-341]. A convenient precipitation of thorium is achieved with methyl oxalate, which first dissolves to form a clear homogeneous solution, and is hydrolysed, and precipitates the thorium [339]. According to some authors, however, the precipitation of thorium with oxalate is not always sufficiently complete [335].

Satisfactory separation from many elements, except Zr, Ti, and Ce, is achieved by precipitating thorium with iodate [331,333], various oxoacids of phosphorus [331,342-355] and selenium [356], and many other reagents [357-359]. A scheme has been described for the separation of thorium from other elements using H_2S. [360].

Very small quantities of thorium can be removed from dilute solution by coprecipitation with calcium oxalate [361], basic titanium phosphate [331,354], zirconium phosphate [331,355], bismuth hypophosphate [329,353], yttrium oxalate, and lanthanum fluoride [329,355]. A method has been described for the coprecipitation of thorium with zirconium using the colorimetric reagent for thorium — thoron [362].

Many methods have been described for separating thorium with organic acids and other organic reagents of high molecular weight [363-429], including sebacic [363-365], picric [336], aryloxyacetic [367-371], 4-aminosalicylic [372-374], benzoic [375,376], *p*- and *o*-aminobenzoic [377], chlorobenzoic [371], nitrobenzoic [379,380], hydroxynaphthoic [381,382], 5,6-benzoquinaldinic [383,384], hydroxytoluic [385], and picrolonic acids [386,387], dibenzoylmethane [388], cupferron [321,389], 8-hydroxyquinoline and its derivatives [386,390-393], phenylarsonic [394-395], phenylphosphinic [396], 7-hydroxycoumarin-4-acetic [397], and phenylglycerol-*o*-carboxylic acids [398,399], cinnamic acid and its analogues [400-402], ferron [363,403], mercaptobenzothiazole, phytic acid, and other reagents [363-407,410,414,426,427].

Thorium is separated completely from the rare-earth elements by precipitation with 8-hydroxyquinoline in the presence of Complexone III. [428] It is precipitated from $< 1.0\ N$ HCl solutions with sodium benzenesulphinate, and Be, Al, Ti, Fe, and the rare-earth and other elements do not interfere [429].

Most of the methods differ little as far as selectivity, convenience, or other factors are concerned, since the precipitation conditions depend chiefly on the properties of the Th^{4+} ion and only slightly on the nature of the reagents used.

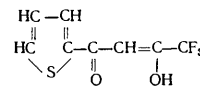
Although methods for the precipitation of thorium are more selective than those for uranium, complete separation of thorium from other elements, particularly those with readily hydrolysable cations, cannot be achieved in one operation, so that it is always necessary to carry out a double precipitation with oxalate, iodate, or, occasionally, phosphate, fluoride, or an organic coprecipitant.

Chromatographic methods can be used to remove thorium from very dilute solutions [430-442], and this is particularly convenient for the analysis of waste liquors, natural waters, and other materials of low thorium content.

A large number of papers are devoted to the separation of thorium from the rare-earth elements [436-442]. A number of cation exchangers absorb thorium and the rare-earth elements completely from almost neutral solutions. The rare-earth elements are then eluted with 1 *N* HCl and the thorium with 3 *N* HCl. [439] Methods involving paper and cellulose column chromatography, which are forms of extraction, have been described.

Extraction of thorium in the form of nitrato compounds is most frequently carried out using mesityl oxide [330,331,340,354] and, less frequently, with other oxygen-containing solvents, such as diethyl ether [443,444], ethyl acetate [157,445], tributyl phosphate [446,447], methyl isobutyl ketone [448] and mixtures of this ketone with tributyl phosphate [912], cyclohexanone [449,450], and other ketones [451-458]. Extremely small quantities of thorium are extracted completely by a mixture of butyl phosphate and methyl acetate [354].

Methods for the extraction of thorium as chelate compounds formed with organic reagents are much less selective. The reagents include thenoyltrifluoroacetone (TTA) (VII), [434,459,460] α-nitroso-β-naphthol [448], acetylacetone, 8-hydroxyquinoline, quinalizarin [488], cupferron [461], quercetin [462], and others [4,88,445,463].



(VII)

C. Methods for the Separation of Plutonium

Precipitation methods have been described chiefly for microquantities of plutonium. Separation from large quantities of other elements is achieved by means of redox cycles [1,464] in which the impurities accompanying plutonium in one or other of its oxidation states show different behaviour when the plutonium is converted to a different oxidation state. Carriers used for the coprecipitation of plutonium include lanthanum fluoride [1,30,464-471], which coprecipitates Pu(III) and Pu(IV) [472], potassium lanthanum sulphate [471,473], certain oxalates and iodates [1], calcium oxalate [467], and bismuth phosphate [470,474-478].

A standard method has been described for the determination of plutonium by coprecipitation with lanthanum fluoride [479]. From strongly acidic solutions, carriers such as zirconium phenylarsonate [465,480] and phosphate [464,477,478] precipitate only Pu(IV), while sodium uranyl acetate precipitates only Pu(VI). [1] Tracer quantities of lanthanides are separated from Pu(VI) by coprecipitation with calcium fluoride [481]. A list of carriers for plutonium in its various oxidation states is given by Hyde [464].

Macro-quantities of plutonium can be separated from some elements by precipitation as hydroxides [470,480,482,483]. The pH values at the start of precipitation of the hydroxides of plutonium cations at concentrations of $\sim 10^{-3}$ M are: Pu(III) ~ 7, Pu(IV) ~ 3, Pu(V) ~ 9, and Pu(VI) ~ 4.5. [282-284] The precipitation of Pu(IV) as the iodate is more selective [467,470,480]. Plutonium can be separated from indium [485], bismuth [486], cadmium [487], and titanium [30] by precipitation as the peroxide at pH 3-4 [480,488], and Pu(III) and Pu(IV) can be separated from uranium, iron, and certain other elements by precipitation of the oxalates in acid medium [1,30,489,490]. Pu(VI) is precipitated as the double carbonates with alkali metals [491,492]. Precipitation of plutonium with 8-hydroxyquinoline gives satisfactory separation from other elements [480,493], and plutonium(III) is precipitated by salicylate at pH 3.5. [30]

The precipitation of plutonium(IV) as various basic salicylates is ~95% complete at pH 4.5 and 99.3–99.9% complete on heating at pH 8. In this case plutonium(IV) is precipitated from solutions containing the element in different oxidation states. Plutonium can also be precipitated with other organic reagents[480].

Chromatographic methods for the separation of plutonium are based on the adsorption of Pu(IV) in its anionic form $PuCl_n^{(n-4)-}$ on Dowex-1 anion-exchange resin at a hydrochloric-acid concentration not less than 2.5 M[464,494,495]. Other actinides in the +4 state are sorbed only at higher HCl concentrations, and separation from uranium is also achieved. Up to 100 mg of plutonium(IV), obtained by oxidising plutonium(III) with a 25-fold excess of sodium nitrite, can be separated completely from most fission products, americium, and other higher actinides, by adsorption on an anion-exchange resin from 7 M nitric acid[496]. Iron appears to be the only common element adsorbed with plutonium[30].

Plutonium can also be separated from other elements with cation exchangers and elution with hydrochloric acid[464] or complex-forming substances such as oxalic acid[169,464,497]. Paper chromatography with n-butanol or ethyl acetate saturated with hydrogen chloride is recommended for the separation of plutonium(III), (IV), and (VI).[490]

Extraction. Like uranium and thorium, plutonium is extracted by many solvents as compounds formed with organic reagents, and from nitrate solutions as salts of a complex nitrato anion by oxygen-containing solvents including diethyl ether, various ketones, and other compounds[30,464,463,498–501]. Separation from most of the lighter elements is achieved in this way. According to Chaikhorskii and Kondratov, extraction with ether separates plutonium completely from neptunium[471]. Dibutyl carbitol extracts Pu(IV) from dilute nitric acid as $HPuO_2(NO_3)_3$.[501] Methods have also been described for the extraction of plutonium(IV) and (VI) with tributyl phosphate[30,464,502–505], solutions of acetylacetone in benzene and other solvents, and TTA.[424,433,460,463–466,464,475,478,506–509]. The extraction of elements with TTA obeys the general laws governing the influence of pH on the tendency of elements to react with reagents of general formula R–OH.[88,510,511] Other readily hydrolysable ions [Pa(V), Fe(III), U(IV), Zr, etc.] are extracted with Pu(IV) from acid solutions. For separation from these elements, the plutonium is reduced to the +3 state, the impurities extracted with TTA, the plutonium in the aqueous layer reoxidised to the +4 state and extracted with a fresh portion of TTA solution in hexone[30].

Plutonium is separated from many radioactive and non-radioactive elements in 1 M nitric acid by extraction with 0.5 M TTA solution in xylene.[479] Further separation from radioactive zirconium, protoactinium, and iron is achieved by re-extracting the plutonium into 10 M nitric acid. Tantalum (0.01–2%) can be separated from plutonium and uranium by extraction with hexone from 6 M sulphuric acid — — 0.4 M fluoride solution[512]. Plutonium can be separated by extraction as amine derivatives[514] and with mixtures of dibutyl ether and carbon tetrachloride[513]. Separation from uranium is achieved by distribution between an organic solvent and a stationary aqueous phase on silica gel[515].

Any extracting agent, for example chloroform, can be used to extract plutonium as the compounds formed with cupferron or neocupferron[464,478,516,517]: in acid medium separation is achieved from uranium, americium, and some other elements. The extraction of plutonium with many other organic reagents has been studied qualitatively[480,518,519].

Other methods. Plutonium is separated from iron and other metals by electrolysis at a mercury cathode[1,30,520]. The element can be deposited electrolytically from weakly acidic, oxalate, or alkaline solutions[470,520–524]. Methods for the deposition of stable coatings of plutonium, neptunium, uranium, and americium have been described[525]. Plutonium is separated from biological materials by mineralisation with hot $HNO_3 + H_2O_2$ mixture[478] and subsequent separation of the plutonium by various methods[478,517]. Filtration of air samples is used to trap plutonium aerosols[526]. The apparatus and necessary precautions for carrying out analytical and other work with plutonium have been described[527,528].

3. METHODS FOR THE DETERMINATION OF URANIUM, THORIUM, AND PLUTONIUM

A. Methods for the Determination of Uranium

Gravimetric methods for the determination of uranium are exactly analogous to the preparation methods described above. Uranium is precipitated by carbonate-free ammonia[176–178], pyridine[180–182], urotropine[179], other organic reagents described above[184,186–208], hydrogen peroxide[4,209,210], ammonium sulphide, and other precipitants[202–208,529]. The precipitates obtained do not as a rule have a definite composition and are ignited at 800°–1050° to U_3O_8.

Careful drying of uranium 8-hydroxyquinolinate at 120°–140° gives a product with composition $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$. According to Ray and others, precipitation of phosphate or ammonium uranyl phosphate yields the stoichiometric product $U_2(P_2O_7)_3 \cdot 4UO_3$.[217]

Uranium can be precipitated with $K_4Fe(CN)_6$ from 1 M KNO_3 solution at pH 2–4 and 50°–60° as $K_4(UO_2)_4[Fe(CN)_6]_3$,[223] and can also be determined accurately in KNO_3 solutions by amperometric titration with $K_4Fe(CN)_6$.[223]. Uranium(VI) is also precipitated by cacodylic acid $(CH_3)_2AsOOH$: a stoichiometric product is obtained by careful heating at 200°.[200,201]

These methods are not selective, and most elements must be removed beforehand. Little is known of more selective methods for precipitating uranium(IV).

Volumetric methods for the determination of uranium include direct titration of U(VI) with powerful reducing agents, and of U(IV) by oxidising agents, indirect redox methods, titration of uranyl solutions with precipitants, complexometric titration, and others[530–583].

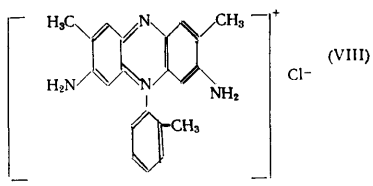
Preliminary reduction of uranium is unnecessary for the direct titration of uranyl solutions with reducing agents, but the instability of the powerful reducing agents used — titanium(III),[530] stannous tin[531], and chromous sulphate[532,533] — reduces the accuracy of the determination.

Methods for the titration of U(IV) are more important. Almost any common oxidising agent can be used, and the choice of titrant and indicator presents no difficulty. Preliminary reduction of the uranium is carried out with powerful reducing agents — titanous chloride[191], stannous tin[531], chromous sulphate[533–536], and solid or liquid amalgams of zinc[538,539], cadmium[540,541], magnesium, aluminium, lead, bismuth, copper, silver, and other metals[533,542–544]. The

reduction is accompanied by contamination of the solutions with ions of the metals used. This does not interfere with the subsequent titration of U(IV), but may be undesirable in some cases. The reduction sometimes yields a mixture of U(IV) and U(III), so that subsequent conversion of U(III) to U(IV) becomes necessary.

An interesting method of reduction involves the use of alcohol. An ethyl-alcohol solution of the uranyl salt, approximately 1 *N* with respect to H_2SO_4, is exposed to direct sunlight or under a mercury lamp for 20–30 min[544]. The uranium is reduced to U(IV) and no foreign ions are introduced. Diethyl ether can be used instead of alcohol[545].

Ceric sulphate[191,434,546-551], potassium dichromate[543,552-554], potassium permanganate[539,553,555-557], ferric sulphate, sodium vanadate[544,545,558,580], and other oxidising agents[4] can be used. Titration with $KMnO_4$ requires no indicator and in other cases the equivalence point may be detected electrometrically[557-559] or with internal indicators such as diphenylamine, diphenylbenzidine, diphenylaminesulphonic acids, etc.[545,548,552,556]. Safranine T(VIII) is used for the oxidation of excess reducing agent by atmospheric oxygen[11]:



(VIII)

The titration of U(IV) is usually fairly easy. When $Fe_2(SO_4)_3$ is used, the titration is carried out in an atmosphere of CO_2 at ~ 70°. The equivalence point is determined potentiometrically with platinum or calomel electrodes[1,30]. Uranium(IV) may be titrated potentiometrically in the presence of U(VI) with $Ti_2(SO_4)_3$,[582] and a special burette for the titration of uranium(IV) in an inert atmosphere has been described[583].

Other volumetric methods for the determination of uranium have been described, including coulometric titration with electrolytically generated Ti(III) ions[571,572], Ce(IV), bromide ions[573], and other reagents[542,574], precipitation of uranium with 8-hydroxyquinoline followed by titration of the precipitate with bromide-bromate mixture[560-562], titration of uranyl salt solutions with sodium phosphate[564,565] or caustic soda[566,568], complexometric titration with Trilon B[509,510], precipitation of uranium with hydrogen peroxide and subsequent titration of the precipitate with $KMnO_4$,[563] and other methods[538,575-577].

Volumetric methods, particularly redox methods, permit the determination of 5–100 γ of uranium[549,558]. The accuracy of the determination equals, and in some cases exceeds, that of gravimetric methods[558,560,578]. The titration of uranium with Trilon B and quercetin indicator permits the determination of 12 γ of uranium with an error of up to 5%.[510]

Physical and physicochemical methods, although less accurate than gravimetric and volumetric methods, have the advantages of high selectivity and rapidity[20]. These methods include polarographic[262,293,584-601], radiometric[35,230,620-615], neutron-activation[602,616], spectral[36,617], X-ray spectral[618-620], the rapid fluorescent X-ray spectral[34,621-626], the highly sensitive microradiographic[627-629], and other methods[630-635].

Polarographic methods are extremely sensitive and only slightly less accurate than chemical methods, and 0.1–10 γ of U can be determined with an error of not more than 3–5%.[20] The use of oscillographic polarography increases the sensitivity by a factor of ~ 30.[20] The selectivity of the polarographic methods is satisfactory, but preliminary separation of other substances is necessary in the determination of uranium in minerals, ores[585,588,589,601], and other materials[586-588]. The selectivity of the methods is greatly increased by using Trilon B to mask other elements[591,592] including Ni, Co, Zn, Mn, Al, Cr, Be, and Ti: interference is caused by Pb and Cu.[592] Problems related to the polarographic determination of uranium have been discussed in detail[4,20].

Fluorescence methods. The almost exclusive ability of the UO_2^{2+}–NaF system to give a bright yellow-green fluorescence under the influence of ultra-violet light was first studied by Nichols and Slattery[636-638], and subsequently Hernegger, Fioletova, Leonova and others developed extremely sensitive methods for the determination of uranium[639-669]. The determination is carried out either visually or with photoelectric fluorimeters[640,641] which increase the sensitivity to 0.001–0.005 γ of uranium in 0.5–2 g of melt, with a mean error of not more than 5–7%.[640,642]

The flux may be pure NaF,[4] or a mixture of 9% NaF, 45.5% Na_2CO_3, and 45.5% K_2CO_3,[4] in which case the melts obtained are stable, homogeneous, and non-hygroscopic; these are important factors in the photometric measurements, while the sensitivity is the same as for pure NaF fluxes. Fluorides of other alkali or alkaline-earth metals have been used as fluxes but do not appear to have any advantages over fluxes based on NaF.[4]

The fluorescence of uranyl compounds in liquids such as concentrated H_3PO_4 and H_2SO_4 solutions[643,644], and organic solvents[645], can also be used for the quantitative determination of uranium.

Fluorescence in uranyl compounds is produced not only by ultra-violet radiation, but also by β-, α-, and cathode rays, protons, and probably neutrons[646]; this may be used to determine uranium and also to measure ionising and neutron radiation.

Interference is caused by strong quenching agents such as Fe, Cr, Co, Pb, Mn, Ni, Pt, Ag, La, Ce, and Ca,[640,647-649] and also by elements which on fusion with NaF exhibit fluorescence, such as Ce, V, Nb, Ta, and Sb.[640,649] Detailed references to elements which interfere in the direct determination of uranium have been given[640,649].

The degree of quenching depends only on the concentration of impurity in the flux and is independent of the UO_2^{2+} : : quenching agent ratio. For fluxes containing up to 1 γ of strong quenching agents (Fe, Cr, Ag) and 10–1000 γ of other quenching agents per g of flux, the decrease in the fluorescence of uranium is almost insignificant[640], so that if a small sample is used, in which the ratio of UO_2^{2+} to other elements is 1 : 10^3–10^6 (uranium content 0.1–0.0001%), direct determination of uranium is still possible without preliminary separation of other elements. In this case decomposition of the specimen is also unnecessary and micro-specimens of minerals are fused directly with the flux[650-652].

The analysis of specimens of complex composition and low uranium content requires preliminary separation of most of the other elements present[279,653-655], or concentration of the uranium, e.g. in sea water with organic coprecipitants, followed by fluorimetric determination[84].

The X-ray-fluorescence method permits the determination

of 0.2–2.0 mg/ml U in 1 ml M of $NaNO_3$ solution[627]. According to Galkin and Feofilov, uranium(III) also exhibits fluorescence in single crystals of CaF_2, SrF_2, and BaF_2.[656]

Many uranium minerals exhibit luminescence, which can be used for their detection and identification[657].

Fluorimetric methods for the determination of uranium have been described in a number of papers[4,22,640], and theoretical problems related to the fluorescence of uranyl compounds have been discussed by Vavilov, Levshin, and others[646,658-661]. The problem of the nature of the luminescent centre in the $NaF-UO_2^{2+}$ system has been discussed by Dobrolyubskaya and others[662-664].

Colorimetric methods. Uranium may be determined from the colour of its simple inorganic salts, e.g. uranium(IV) phosphate in 40% H_3PO_4 (λ, 660 mμ),[670] uranyl perchlorate in $HClO_4$ (λ, 415–420 mμ),[671-673] uranyl sulphate in H_2SO_4 (λ, 420–430 mμ),[674-676] and others[540]. A method has been described for the direct spectrophotometric determination of uranium in sulphate or carbonate solutions, based on the characteristic absorption of the complexes in the ultra-violet range. Methods using the colour of uranium salts are highly selective but the sensitivity is insufficient (up to 0.5–5 mg/ml U).

A number of methods have been described for the photometric determination of uranium with oxygen- and sulphur-containing reagents. The simple and convenient method using H_2O_2 in Na_2CO_3 solution is not very sensitive[678-689]. The selectivity is satisfactory, and can be increased further by using a medium of H_2O_2 + NaOH + Na_2CO_3 at lower H_2O_2 concentrations[687]. Interference from V, Mo, and W is almost completely eliminated, but some interference is caused by bicarbonate[679]. A number of authors have studied the composition of the coloured peroxo compounds of uranium[683,684].

In some cases hydrogen peroxide is also used to mask UO_2^{2+} in the complexometric titration at pH 10[211] and in the photometric determination with arsenazo reagents[146].

Uranium may also be determined with KSCN in aqueous solution[690-696], and in mixtures containing acetone, alcohol, or ethylene glycol monobutyl ether[289,697,698]. The selectivity of the method is much higher in the presence of acetone or alcohol; relatively large quantities of Th, Zr, Sn, Hg, Mn as well as sulphate, phosphate and acetate do not interfere; Fe(III) is reduced with ascorbic acid[698] or stannous chloride[697].

An advantage of the thiocyanate method is that the determination can be carried out over a wide range of acidity (0.1–2.0 *N* HCl or HNO_3). The method is insufficiently sensitive (~20–40 γ/ml U). The use of $K_4Fe(CN)_6$ provides a more sensitive method[111,218,699-701], and permits the determination of 10–100 γ of U in 25 ml with an error of 3–5%, but it is insufficiently selective and it is almost always necessary to remove other elements, as well as acetates, oxalates, citrates, and other complex-forming substances[702]. Methods have been described for the determination of uranium in ores, minerals[218], and other materials[111]. At high uranium concentrations, or in the presence of KNO_3, $K_4Fe(CN)_6$ gives a precipitate, which makes the colorimetric determination impossible[703,704]. The composition of the products formed by uranyl ions with potassium ferro- and ferricyanide has been discussed[223,705].

The chromophoric action of uranium also forms the basis of analytical methods using weakly-coloured or colourless organic reagents[124,706-765], including salicylic, aminosalicylic, and sulphosalicylic acids[124,128,706-712], salicylamide[713], salicylaldoxime[714,715], salicylhydroxamic acid[716], Tiron [1,2,4,6-$C_6H_2(OH)_2(SO_3H)_2$]* [717], gallic[732], and chromotropic acids[716-720], dibenzoylmethane and its analogues in aqueous or organic media[285,726-731], 2-acetoacetylpyridine[734,735], R-salt and nitroso-R-salt[721], 8-hydroxyquinoline[116,607,722], ammonium thioglycollate[723-725], reductone[733], isatin-β-oxime[737-743], sodium azide[746], various naphthosulphonic acids[202,747], tannin[182,732], morin[748-751], morellin[752,753], ferron[765], and others[754-765].

All these methods using organic reagents have approximately the same sensitivity (~5 γ/ml). The selectivity is not high, but may be increased using Trilon B to mask interfering elements. According to Pribil, Almashi, and others, Cu, Fe, Ni, Co, Mn, Bi, Al, Th and some other elements do not interfere in the determination of uranium with dibenzoylmethane, morin, or salicylaldoxime in the presence of Trilon B.[70-77]

Methods using coloured organic reagents have recently become more important. Arsenazo, the most widely used[128,143,145,146,540,766,767], is suitable for the determination of both U(VI) and U(IV). The determination of U(VI) is not selective: Th, Zr, Ti, Al, Fe, and the rare-earth and other elements interfere and must be removed. The interference of small amounts of other elements can be eliminated by adding Trilon B or by using the fact that the UO_2^{2+} : : arsenazo complex is decomposed by adding H_2O_2.[146]

The determination of U(IV) is more selective, and only the readily hydrolysable elements Zr, T, and Th interfere. Phosphate, fluoride, and oxalate mask the uranium in both cases. The sensitivity of the reaction is 0.05–0.1 γ/ml U.

U(VI) can be determined with urotropine at pH 4.5–6. The light absorption is measured with a spectrophotometer at 620 mμ or with a photocolorimeter and a red filter. U(IV) is determined in more strongly acidic medium — 0.05–0.2 *N* HCl.[146] Banks and Fritz have described methods for the determination of small amounts of rare-earth elements in uranium[768,769]. Thoron, an analogue of arsenazo, has been proposed for the determination of U(IV).[128] The reaction is also carried out in acid medium (0.1–0.3 *N* HCl) and only Zr, Ti, and Th interfere. The sensitivity of the method is 0.1–0.2 γ/ml U. Arsenazo II has been suggested for the determination of UO_2^{2+}. The sensitivity does not exceed that of the reaction with arsenazo I, but the selectivity is much higher[147].

A number of other coloured reagents have been recommended, including alizarin S and its analogues[770,771], aluminon[772], 1-(2-pyridylazo)-2-naphthol[294,773], and other azo-dyes[128,774]. Nitrilotriacetic acid, KCN, or Trilon B have been used to mask Cu, Zn, Ni, Hg, Fe, Zr, and Th in the determination of uranium with 1-(2-pyridylazo)-2-naphthol[773]. The determination can also be carried out directly after extraction in tributyl phosphate–$CHCl_3$ with the addition of the reagent and pyridine[775,776].

There is an indirect colorimetric method for the determination of uranium, consisting in the oxidation of U(IV) to U(VI) with Fe(III) salts and subsequent determination of the Fe(II) formed with *o*-phenanthroline or dimethylglyoxime[775,776].

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* Tiron is actually the name given to the disodium salt of 1,2-dihydroxybenzene-3,5-disulphonic acid (Ed. of Translation).

B. Methods for the Determination of Thorium

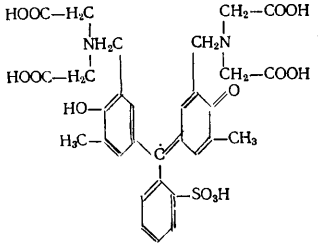
Gravimetric methods for the determination of thorium are based on the precipitation reactions already described. In the hydrolytic precipitation of thorium with bases[321-328] or organic acids[363-426], the metals Zr, Ti, Fe, U and large quantities of rare-earth elements must be absent.

In the absence of rare-earth elements and calcium, thorium is precipitated by oxalate as $Th(C_2O_4)_2 . 6H_2O$[333-341], or by fluoride as $ThF_4 . 8H_2O$.[329] In the absence of Ti and Zr, thorium is precipitated as the iodate[331,333]. In most cases the precipitates obtained are ignited to ThO_2. Precipitation of thorium with phytic acid and ignition of the precipitate yields stoichiometric $Th(PO_3)_4$.[162].

After precipitation of thorium with hydroxyquinoline or mercaptobenzothiazole, the precipitates may be dried at 105°–120° and weighed as $Th(C_9H_6NO)_4 . C_9H_6NOH$ [4,426] and $Th(C_7H_4NS_2)_4$ [777] respectively. Precipitation of thorium with sodium benzenesulphinate and drying at 110° gives stoichiometric $Th(C_6H_5SO_2)_4$.[429] Reviews of gravimetric methods for the determination of thorium have been given[4,29].

Volumetric methods for the determination of thorium are more rapid and convenient. The indirect iodate–thiosulphate method developed by Chernikhov and others is of particular interest[222,355,778,779]. It is based on the precipitation of potassium thorium iodate $4Th(IO_3)_4 . KIO_3 . 18H_2O$ from nitric-acid solution[222,331,333] with subsequent dissolution of the precipitate in acidified potassium iodide solution and titration of the liberated iodine with sodium thiosulphate. The method is fairly selective: Zr, Ti, and large quantities of Bi and the rare-earth elements must be absent.

Recently-developed complexometric methods for the determination of thorium are very rapid and convenient. Trilon B,[780-804] KF,[790,805] or $Na_2C_2O_4$,[790] can be used and the indicators are reagents which give distinct colour changes with thorium: alizarin S,[128-130,780,798] various azo-dyes, particularly those based on chromotropic acid or R-acid[784], 2,7-dinitrosochromotropic acid[785], Eriochrome Cyanine R,[128] xylenol orange (IX),[799,801] ferroin[803], pyrocatechol violet[787,789,800,803], and others[786,788,796]. Physicochemical methods are also used to detect the equivalence point[791,792].



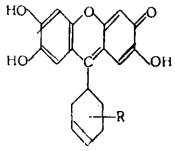
(IX)

A method has been suggested for the determination of micro-quantities of thorium in metallic uranium by coprecipitation with lanthanum fluoride followed by titration with EDTA and Eriochrome Cyanine RC indicator[806]. All elements which react with the complexone, or give colour reactions with the indicators at the experimental pH, interfere. A critical review of complexometric methods for the determination of thorium has been given by Přibil[807].

Other volumetric methods include amperometric titration of thorium with ammonium molybdate[808-810], titration of thorium hydroxyquinolinate with bromine[393], potassium permanganate titration of thorium oxalate[811,812] or the excess oxalic acid after precipitation of thorium[812,813] and others[810,814].

Physical and physicochemical methods include spectral[38,815-820], X-ray spectral[38,619], X-ray fluorescent spectral[623,821], radiochemical[37,612-614,822-824], neutron-activation[825,826], indirect polarographic[827-831], and other methods[4,832]. One indirect polarographic method involves treatment of a standard solution of the ethylenediaminetetraacetato complex of lead with the test thorium solution, followed by polarographic determination of the Pb, which is displaced from the complex by the thorium[831]. An indirect radiochemical method involves precipitation of the thorium with pyrophosphate labelled with radioactive phosphorus and measurement of the activity of the excess pyrophosphate in the filtrate[349].

Thorium can be determined from the fluorescence with various flavones, morin, or, in alcoholic solution, with 1-amino-4-hydroxyanthraquinone[833,834]. Many elements do not interfere, but the reaction is not so selective as the fluorescent reaction of uranyl ions in fused NaF. The complex formed by thorium with 2,3,7-trihydroxy-6-fluorone is decomposed with sulphate in an indirect fluorescence method for the determination of thorium: the liberated reagent exhibits fluorescence[835].



Photometric and colorimetric methods. Most appear to be based on the use of thoron (APANS),[329,330,361,435,459,766,836-849,912] first suggested in 1941 by Kuznetsov[143,145]. The error in these methods is 1.5–2%. The determination is carried out at pH 0.7–1.2: UO_2^{2+}, Fe(II), Al, Pb, and other elements do not interfere, but Zr, Ti, and anions which mask thorium cause difficulty.

Thorium may also be determined with arsenazo[449,450,540,766,850,851]. The reaction is more sensitive, but the influence of other elements is more marked. Zaikovskii and Gerkhard have described a method for determining thorium with arsenazo in the presence of Zr and Ti, which are masked with tartaric acid[852].

Other reagents proposed for the determination of thorium include alizarin[853-856], quinalizarin[857], methyl red[858,859], quercetin[434,462,860,861], morellin[862], nitroso-R-salt[863], pyrocatecholsulphonephthalein[864], morin[865], Carmine Red[866], 2,7-dinitrosochromotropic acid[867], hematein[868], 2,5-dihydroxyquinone in methanol[869], various azo-dyes, mostly based on chromotropic acid[870-874], and other reagents[875-877]. The sensitivity of these methods is 1–10 γ/ml Th, and interference is shown by the same elements as in the case of arsenazo and thoron, i.e. Zr, Ti, Fe(III), large quantities of Al, UO_2^{2+}, and rare-earth elements, and by anions such as sulphate, phosphate, and fluoride which mask thorium.

Indirect colorimetric and nephelometric methods[331,345,878-880] have no advantages over direct colorimetric methods and are not widely used.

C. Methods for the Determination of Plutonium

Gravimetric methods. Plutonium is generally determined gravimetrically as the dioxide[480], obtained by igniting plutonium hydroxide[480], or the precipitates obtained with organic compounds[480,489,490,493] or H_2O_2.[480,483]. Thermogravimetric study of many plutonium compounds has shown that plutonium dioxide is formed above 600°–650°.[881] The properties of plutonium dioxide have been studied[882,883], and a recent detailed study has shown that the weight of the product obtained at 900° differs from the theoretical by between +0.1% and +0.5%.[884] The weight of plutonium dioxide obtained by ignition at a given temperature is constant. The weight corresponds closely to the stoichiometric composition PuO_2 after ignition at 1100°–1200° in air. At higher temperatures lower oxides are formed[885,886]. In some cases, plutonium dioxide may be oxidised to $PuO_{2.1}$. Plutonium(IV) may also be determined gravimetrically as the sulphate or iodate[480].

Volumetric methods. These are based chiefly on redox reactions. Pu(III) is titrated in sulphuric-acid medium with cerium(IV), potentiometrically or with ferroin indicator[887]. The error in the determination of 2–10 mg of plutonium is 0.1–0.25%. It is reported that plutonium may be determined by titration with potassium permanganate, or by thiosulphate titration of the iodine liberated from iodide by plutonium(IV) in sulphuric acid[480].

Plutonium may be oxidised to the +6 state by perchloric acid followed by reduction with excess Fe(II), which is then titrated potentiometrically with standard Ce(IV) sulphate solution[30,34]. This method permits the determination of 400–500 mg of plutonium with an error of 0.03%. Iron does not interfere, but Cr, V, and Mo should be absent.

Plutonium in the +3, +4, and +6 states forms stable complexes with ethylenediaminetetraacetic acid[30,34,888]. The instability constant of the Pu(IV) complex is $\sim 10^{26}$ and that for Pu(III) $\sim 10^{16}$. A volumetric method has been recommended for the determination of Pu(III), based on the back titration of excess complexone with thorium at pH 2.5 in the presence of sodium alizarinsulphonate and methylene blue (internal light filter)[889]. The error in the determination of 10 mg of Pu is ~1%.

Physical and physicochemical methods. The radiochemical method appears to be most widely used[30, 34,509,890-893]. Various methods for preparing specimens for α-counting have been described[893-895] including electrolysis[492,520-523]. When less than 0.01 g/litre Pu and high concentrations of other salts are present, preliminary separation of the plutonium is necessary. In other cases the solution is diluted and an aliquot portion evaporated on the target[30,34]. A radiometric method for the determination of Np^{239} and Pu^{239} in a homogeneous reactor has been described[896]. The results of the radiochemical analysis depend on the isotopic composition of the plutonium[30-34], which can be found by measuring the α-particle energy or by mass-spectrometry[30,34,897].

An improved method for the determination of micro-quantities of plutonium in water[898], and a method for the radiometric determination of plutonium after separation by coprecipitation or extraction[479] have been described. Autoradiography may also be used[470].

The oxidation state of plutonium in micro-quantities can be determined by coprecipitation of the different states with carriers[1], or, in milligram quantities, from the spectra of the solutions[899].

According to Allison, the Pu(III) bands at 602 mμ can be used for the spectrophotometric determination of plutonium with an error of 1%[30,34]. According to other data, 8–14 mg of plutonium(III) can be detected with an error of 0.1% by differential spectrophotometry at 565 mμ.[174] The plutonium is reduced by 5% hydroxylamine hydrochloride in 1 M HCl. No interference is caused by a tenfold excess of thorium, uranium, calcium or cerium, by an equal quantity of ferrous iron (in the presence of stannous chloride), or by less than equal quantities of aluminium and zirconium. Connick et al. recommend the use of the following main analytical absorption bands (the molar extinction coefficients are given in brackets): Pu(III) 560 mμ (36.1), 600 (35.3), 900 (19.3); Pu(IV) 470 mμ (49.6), 655 (34.4), 730 (14.6), 815 (19.6); Pu(VI) 833 mμ (~300), 953 (19.9), 983 (8.9).[899] Analogous spectra are characteristic of crystals of plutonium salts[900] The molar extinction coefficients of plutonium in solution depend on the temperatue, pH, and the nature and concentration of anions present[34,899]; the above data relate to solutions in 0.5 M HCl or HNO_3.

For the coulometric determination of plutonium, Dreeben has recommended electrolytic reduction to the +3 state followed by oxidation with electrolytically generated ceric ions in nitric acid–sulphanilic acid medium[901].

Brunstad, Carson, and others have proposed a method for the oxidation of plutonium to Pu(VI) with potassium permanganate, excess of which is removed by heating with formic acid. The Pu(VI) formed is then reduced in sulphuric acid–phosphoric acid medium by electrolytically generated Fe^{2+} ions[902,903]. Plutonium can be detected coulometrically in 0.5–10 mg amounts with an error of 0.5–2%, and 3 γ of plutonium with an error of 5%[31,34]. Milligram quantities of Pu(IV) are determined by reduction with zinc amalgam followed by titration with Ce(IV) sulphate[904]. Plutonium can be determined with an error of 0.1–1% in 0.05–2 mg amounts by coulometry at controlled potential with a mercury or platinum electrode[905,906]. Direct determination of plutonium is possible in the solutions obtained by treatment of nuclear fuel.

The quantitative polarographic determination of plutonium can be carried out using the clearly-defined wave for the reversible reaction in oxalate solutions at pH 3.5–6.[907] Plutonium(III) in hydrochloric-acid solution containing hydroxylamine does not interfere in the polarographic determination of uranium, vanadium, and titanium[30,34]. Methods have been described for the polarographic reduction of Pu(IV) at an Hg cathode in the presence of complex-forming substances[908].

The concentration of plutonium in pure concentrated solutions may be found from the X-ray absorption[30,34], with an error not exceeding 0.15%.

Plutonium can be determined spectrographically using the lines 2972.54 Å, 2994.07 Å, 3000.53 Å, and 3989.78 Å.[891,909]

Colorimetric methods. Only a few have been described. Plutonium(IV) forms brown and red peroxo complexes in acid solutions and reacts with ferron at pH 2.5–8[519]: Pu(IV) can also be determined from the red colour obtained with sodium alizarinsulphonate in formic-acid buffer at pH ~3.[910] Most other elements are removed by electrolysis at a mercury cathode: oxalate, tartrate, and other anions interfere.

Plutonium(IV) in 5–100 γ amounts can be determined with thoron in 0.05–0.25 N HNO_3 or HCl. Interference is caused by U(IV), Th, Zr, to a lesser extent by Ce(III), Fe(III),

U(VI), and by anions which form complexes with Pu. The influence of F^- ions can be eliminated by adding aluminium nitrate. The error in the determination of 100 γ of Pu is ±1% [911].

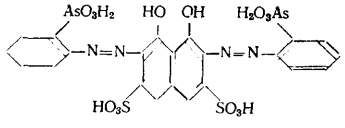
It should be possible, by analogy with U(IV) and Th, to determine Pu(IV) with reagents such as arsenazo I, arsenazo II, and thoron II, but no such methods have been described.

NOTE ADDED IN PROOF

Since this article was prepared, a number of new papers have appeared, and we shall mention the most important of these. A monograph by Lipilina [913] is devoted to the chemistry of uranyl compounds. A review by Ryabchikov and Golbraikh gives data on the chemistry of thorium and its compounds [914], and a fluorimetric method has been described for the determination of uranium in zircon, permitting the determination of 0.0005% of U. [915].

A number of new photometric methods have been published. Uranium can be determined directly from the colour of its compounds in the organic phase after extraction with TTA [916] or a mixture of tributyl phosphate and CCl_4. [917] Everest and Martin have described a method based on the extraction of thorium with tributyl phosphate in isobutyl ketone followed by determination with thoron [918]. The selectivity of the determination of thorium with thoron II is increased by carrying out the determination in strongly acidic solution containing oxalic acid to combine with Zr. [919] A rapid method has been developed for the determination of thorium in monazite using arsenazo II. [920] Zirconium is masked with phosphate, and other elements have almost no effect. Methods have been described for the determination of uranium with arsenazo I [921] and arsenazo II [922]: in the latter method the uranium is separated beforehand by extraction with so-called "fusible extracting agents" — a melt of paraffin and cyclohexanone. The syntheses of arsenazo II and thoron II have been described [925].

The reagent arsenazo III, proposed by Savvin, can be used for the determination of a number of elements, including thorium and uranium [923], with which the reagent forms very stable intensely coloured green complexes.



Solutions of the reagent are pink. The reagent reacts with thorium over a wide range of acidity: 0.01–10 M HCl, HNO_3, or H_2SO_4; with UO_2^{2+} the colour is produced at pH 1–3. Thorium can be determined conveniently in 3–6 *N* HCl in the presence of oxalic acid to mask zirconium. Other elements do not interfere [913]. A method for the determination of thorium in zircon with arsenazo III has been described [924].

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PROGRESS IN THE SYNTHESIS OF HIGH POLYMERS

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I. INTRODUCTION

The chemistry of high polymers is at the present time one of the most vigorously developing branches of chemical science. The most rapid progress is in the synthetic chemistry of high polymers, a field in which advances have been especially evident in recent times.

This rapid development is explained by the fact that advances in the synthetic chemistry of high polymers ensure the development of such important branches of technology as plastics, synthetic rubber, synthetic fibres, and synthetic film-forming materials. In its turn, the production of these materials plays an important part in the development of such branches of industry as aviation, automobile, electrical and radio engineering, machinery manufacture, building construction, etc. On the one hand, new synthetic polymers provide new materials with high thermal stability, strength, etc., and on the other, the production of synthetic materials enables a hugh quantity of

cheap materials to be obtained for industries producing consumer goods.

The first synthetic polymeric product was phenol–formaldehyde resin, obtained by Baekeland[1] at the beginning of the present century. Since then a great industry of synthetic high polymers has grown up, and is developing rapidly.

The rapid growth in the production of polymeric materials can be seen from Table 1, which gives figures for their world production (apart from the USSR and the People's Democracies). It is interesting that this rapid growth in production is due mainly to the development of the manufacture of various synthetic polymeric materials, as can be seen from Table 2, which gives comparative figures for the increase in the production of various natural and synthetic polymers, starting from 1940. Table 2 shows that the total production of synthetic polymers in 1957 had increased 5.38 times, whereas the production of the natural materials had remained almost at the 1940 level (an increase of only 16%).

The scale of production of various polymeric materials is nowadays quite large: for example, Table 3 gives comparative data for the production of non-ferrous metals and plastics. In comparing metals and plastics it is necessary to introduce a correction for the density of the material, as is done in Table 3. Comparison by volume instead of weight then shows that the production of plastics had by 1956 already exceeded the total production of non-ferrous metals.

From the rates of increase in the production of polymers and ferrous metals, Semenov[6] estimates that within 15–20 years the scale of production of polymers will have reached that of the smelting of ferrous metals. The rapid growth in production is paralleled by a similarly rapid growth in the volume of scientific research on the synthesis of high polymers.

The object of the present review is to appraise advances which are occurring in the development of synthetic methods for preparing high polymers.

Recently more than a thousand papers and patents on synthetic high polymers have been published annually[6]. It is evidently impossible to review the whole of this copious material within the limits of the present paper. The review is therefore confined to the publications of the past two or three years. Even here, however, the superabundance of published results has made it necessary to select only those that appeared to be of practical interest.

TABLE 1. Growth of world production of various polymeric materials[2-5] (in thousands of tons).

Material	Year		
	1950	1955	1957
Fibres (natural and artificial)	8648	12343	12419
Plastics	1500	3100	4000
Rubbers (natural and synthetic)	2434	3045	3280
Paints and varnishes	—	—	4562
Total			24261

TABLE 2. Growth in the production of various forms of polymeric materials[2] (in thousands of tons).

Material	Year					1957 production as a percentage of	
	1940	1946	1950	1956	1957	1940	1950
Synthetic polymeric materials							
Synthetic rubber	43	844	583	1303	1350	3134	232
Artificiol and synthetic fibres	1106	760	1624	2560	2700	244	166
Plastics	350	720	1530	3600	4000	1140	261
Total	1499	2324	3737	7463	8050	538	216
Natural polymeric materials							
Natural rubber	1437	851	1890	1915	1930	135	102
Cotton	6100	4300	5400	7200	6700	110	124
Wool	1130	940	1050	1140	1180	104	112
Total	8667	6091	8340	10255	9810	116	113

TABLE 3. Production of non-ferrous metals and of plastics[2].

Material	Year			1956 production as a percentage	
	1940	1950	1956	1940	1950
Aluminium	710	1310	2894	408	221
Copper	2330	2290	3016	129	132
Zinc	1540	1860	2488	162	134
Lead	1640	1560	1861	113	119
Tin	232	177	180	77	102
Total, 10^3 tons	6452	7197	10430	162	145
$10^3 m^3$	919	1166	1951	215	167
Plastics, 10^3 tons	350	1530	3600	1028	236
$10^3 m^3$	259	1133	2667		
Ratio of plastics to non-ferrous metals wt.%	5.4	21.3	34.5		
vol.%	28.2	97.2	137.0		

II. NEW METHODS FOR THE SYNTHESIS OF HIGH POLYMERS

The growth in the production of polymers is based on scientific research which is developing equally rapidly. As a result, many new synthetic methods for polymers have been discovered, and many thousands of new high polymers have been prepared.

We shall point out only the main advances in the field of new methods for the synthesis of polymers. Among them are the discovery by Ziegler and Natta of new catalysts for the polymerisation of olefinic hydrocarbons, which have enabled stereoregular polymers to be prepared; the discovery of methods of preparing graft and block copolymers; the discovery of the cyclopolymerisation of diene monomers; the application of dehydrogenation polymerisation; the discovery of the polyrecombination of various compounds; the use of polycondensation at the interface between two immiscible liquids; the development of the hydrolytic polymerisation of cyclic compounds; and the preparation of co-ordinated-chain polymers. Each of these cases will be considered briefly.

A. Stereospecific Polymerisation

We shall consider first the work of Ziegler, who discovered a new method of synthesising polyethylene. The

catalysts which he found[7], consisting of a trialkylaluminium and titanium tetrachloride, enabled the polymerisation of ethylene to be carried out at ordinary pressures[8,9].

1. Mechanism of the reaction. Polymerisation occurs as an ionic process. An ethylene molecule adds on to a C–Al bond in the original catalyst or in the growing chain according to the scheme $Al-R + C_2H_4 \rightarrow Al-[CH_2]_2-R$, etc. This reaction is characterised by the absence of free-radical processes, which would lead to branching of the polymers being formed. Low-pressure polyethylene therefore contains no branched macromolecules, in contrast to high-pressure polyethylene, which has an extremely branched macromolecule, as is shown in Fig. 17.

Use of $TiCl_3$ and trialkylaluminium compounds enabled Natta to prepare stereoregular polymers of propene and other α-olefins[10,11]. The reaction mechanism for the formation of stereoregular polymers is as follows. The start of chain growth occurs by addition of a monomer molecule to a metal atom in the catalyst and one of the radicals according to the equation

$$[X_nMR \rightleftarrows X_nM + R] + CH_2{=}CHR_1 \rightarrow$$
$$\rightarrow [X_nMCH_2CH(R_1)R \rightleftarrows X_nM\overset{+}{C}H_2CH(R_1)R].$$

The reaction occurs in this case as an anionic polymerisation, in which the growing molecule is combined with aluminium and not with titanium. Chain propagation and termination occur according to the scheme shown in Fig. 1.

D'Alelio and Miranda[12] consider that the catalyst system consisting of a trialkylaluminium and titanium tetrachloride can act by a cationic mechanism in the presence of an excess of the latter component, and by an anionic mechanism with excess of the trialkylaluminium.

Natta[13] suggests the following scheme of individual stages in the process of polymerisation. The first stage in the reaction, initiation, occurs as follows:

$$[cat]^{(+)}{-}R^{(-)} + CH_2{=}CH{-}CH_3 \rightarrow [cat]^{(+)}{-}^{(-)}CH_2\underset{\displaystyle CH_3}{CH}{-}R\ .$$

Chain propagation then continues according to the scheme

$$[cat]^{(+)}{-}CH_2\underset{\displaystyle CH_3}{CH}(CH_2{-}CHCH_3)_{n-1}R + CH_2{=}CHCH_3 \rightarrow$$
$$\rightarrow [cat]^{(+)}{-}^{(-)}CH_2\underset{\displaystyle CH_3}{CH}(CH_2CHCH_3)_nR\ .$$

Chain termination can occur in several ways: (*a*) unimolecular termination; (*b*) first-order termination with respect to monomer; and (*c*) termination by the aluminium alkyl.

(*a*) Unimolecular termination, which consists in the splitting off of catalyst:

$$[cat]^{(+)}{-}^{(-)}CH_2\underset{\displaystyle CH_3}{CH}(CH_2CHCH_3)_nR \rightarrow [cat]^{(+)}{-}^{(-)}H + CH_2{=}\underset{\displaystyle CH_3}{C}(CH_2CHCH_3)_nR.$$

(*b*) First-order termination with respect to monomer, consisting in chain transfer via the monomer:

$$[cat]^{(+)}{-}^{(-)}CH_2\underset{\displaystyle CH_3}{CH}(CH_2CHCH_3)_nR + CH_2{=}CHCH_3 \rightarrow$$
$$\rightarrow [cat.]^{(+)}{-}^{(-)}CH_2CH_2CH_3 + CH_2{=}\underset{\displaystyle CH_3}{C}(CH_2CHCH_3)_nR$$

(*c*) Termination by the aluminium alkyl, consisting of the exchange of alkyl groups between the growing chain and the aluminium alkyl:

$$[cat]^{(+)}{-}^{(-)}CH_2\underset{\displaystyle CH_3}{CH}(CH_2CHCH_3)_nR + R'AlR_2' \rightarrow$$
$$\rightarrow [cat.]^{(+)}{-}^{(-)}R' + R_2AlCH_2\underset{\displaystyle CH_3}{CH}(CH_2CHCH_3)_nR$$

or

$$TiCl_nAlY_2P + AlR_3 \rightarrow TiCl_nAlR_3 + AlY_2P,$$

where Y is the alkyl and P the polymer chain.

Cooper and Rose[14] give the following reaction scheme, in which the first stage is adsorption of ethylene on the surface of titanium:

$$Ti^{2+} + \overset{\displaystyle CH_2}{\underset{\displaystyle CH_2}{\|}} + ClAlR_3 \rightarrow Ti^{+}CH_2CH_2R + AlR_2Cl.$$

Polymerisation then proceeds by a monomer molecule breaking into the Ti–C bond:

$$Ti^{+}CH_2CH_2R + nC_2H_4 \rightarrow Ti^{+}(CH_2CH_2)_nCH_2CH_2R.$$

Chain transfer is then possible via ethylene:

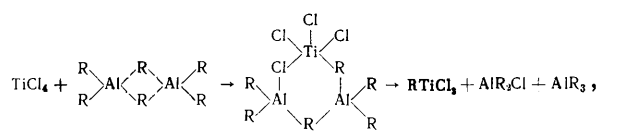
$$Ti^{+}CH_2CH_2(CH_2CH_2)_nR + CH_2{=}CH_2 \rightarrow Ti^{+}CH_2CH_3 + CH_2{=}CH(CH_2CH_2)_nR.$$

In this case the polymer will contain the same end-groups as in Natta's scheme.

Another mechanism is possible, with formation of a hydride ion:

$$Ti^{2+} + CH_2{=}CH_2 \rightarrow Ti^{3+}CH{=}CH_2 + H^-\ ,$$
$$Ti^{3+}CH{=}CH_2 + nC_2H_4 \rightarrow Ti^{3+}(CH_2CH_2)_nCH{=}CH_2\ ,$$
$$Al{-}R_2Cl + Ti^{3+}(CH_2CH_2)_nCH{=}CH_2 \rightarrow Ti^{2+} + R(CH_2CH_2)_nCH{=}CH_2 + AlR_2Cl.$$

There exist other views on the reaction mechanism. Thus Badin[15] suggests the following mechanism:



$$RTiCl_3 \rightarrow R + TiCl_3.$$

He considers that the radical which is formed is able to initiate the polymerisation reaction. Further, the resulting $TiCl_3$ also can activate the double bond of the olefin.

The following mechanism is possible for the polymerisation with a catalyst consisting of titanium tetrachloride and phenyllithium:

$$TiCl_4 + LiC_6H_5 \rightarrow C_6H_5TiCl_3 + LiCl\ ,$$
$$C_6H_5TiCl_3 \rightarrow C_6H_5 + TiCl_3.$$

The presence of phenyl groups in the resulting polymer was actually detected by infra-red spectroscopy[15]. Study of the infra-red spectra of the $TiCl_4 + (CH_3)_2AlCl$ system has shown that the two components react to form CH_3TiCl_3:[18]

$$2TiCl_4 + Al_2(CH_3)_4Cl_2 \rightleftarrows 2CH_3TiCl_3 + Al_2(CH_3)_2Cl_4.$$

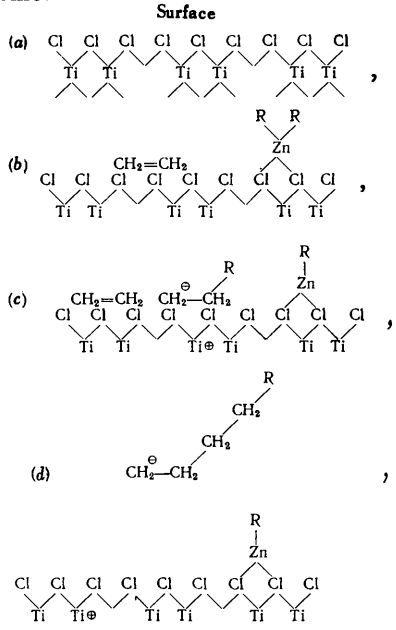
Beerman[17] isolated CH_3TiCl_3 (dark-violet crystals, m.p. 28.5°) by the action of $(CH_3)_3Al$ on $TiCl_4$, and showed that in

the presence of $TiCl_3$ it is more active than the $AlR_3 + TiCl_4$ system in catalysing the polymerisation of ethylene.

Gilchrist[19] gives a different scheme for the action of a Ziegler catalyst. He considers that polymerisation occurs at the surface of $TiCl_3$ crystals formed by the reduction of $TiCl_4$ by the reaction

$$TiCl_4 + Zn(C_4H_9)_2 \rightarrow TiCl_3 + Zn(C_4H_9)Cl + C_4H_9-$$

$TiCl_3$ separates in the form of particles the surface layer of which consists of chlorine atoms. Ethylene and $Zn(C_4H_9)_2$ undergo equilibrium adsorption on these particles, and a slow initiation reaction occurs. Chain growth occurs at a rate which is proportional to the amount of ethylene adsorbed on the surface, the positive charge travelling along the surface behind the negative charge, as is shown in the following scheme:



In this mechanism chain growth occurs along the surface, and not from a single centre represented by the organometallic compound. Gilchrist[19] finds support for his scheme in the fact that products of the radiolysis of $TiCl_4$ bring about the polymerisation of ethylene in the absence of other substances, just as a mixture of ethylene and $TiCl_4$ vapour yields low-pressure polyethylene on ultra-violet irradiation.

We see that there is at present no single viewpoint on the mechanism of stereospecific polymerisation: this is due to the complexity of this process and the difficulty of investigating it, as has been indicated in other reviews[16,20,22].

Apart from catalysts belonging to the $TiCl_4 + AlR_3$ system, a number of others have been proposed, e.g. $CH_3TiCl_3 + TiCl_3$,[17] $TiCl_4 + C_6H_5Li$,[15] $TiCl_4 + C_5H_{11}Na$,[21] $TiCl_4 + RLi$,[22,23] $TiCl_3 + AlR_3$,[11] $TiCl_4 + Zn(C_4H_9)_2$,[19] and $HLi + AlCl_3 + TiCl_4$.[24]

A common defect of these catalysts is their insolubility in the reaction mixture and the difficulties associated with their removal from the resulting polymer. Therefore soluble catalysts are of great interest. The first of them consists of tetraphenyltin, aluminium chloride, and vanadium trichloride, $(C_6H_5)_4Sn + AlCl_3 + VCl_3$,[25] and the second of dicyclopentadienyltitanium dichloride and diethylaluminium chloride, $(C_5H_5)_2TiCl_2 + (C_2H_5)_2AlCl$.[26] Bawn and Symcox[27] prepared a soluble catalyst for the polymerisation of ethylene from tetrabutyl orthotitanate and triethylaluminium, $Ti(OC_4H_9)_4 + Al(C_2H_5)_3$.

The use of soluble catalysts enables the reaction to be carried out in a homogeneous system with a lower consumption of catalyst and yields an unbranched polyethylene with a narrow molecular-weight distribution. Boldyrev et al.[28] have shown that titanium tetrachloride is reduced by a trialkylaluminium to Ti^{3+}, Ti^{2+}, and even metallic titanium. The extent of reduction depends on the nature of the alkylaluminium: $Al(C_2H_5)_3$ is the most vigorous reducing agent. Natta[29] was able to control the molecular weight of the polymer by adding various substances, $Zn(C_2H_5)_2$, HCl, $CH(C_6H_5)_3$, and C_2H_5Br. The use of hydrogen (under pressure) lowers, and that of oxygen-containing catalysts raises, the molecular weight of the polymers.

Kargin et al.[31] have shown that when the catalysts are very finely divided, which is achieved by the molecular-beam method, polymerisation of styrene, α-methylstyrene, methyl methacrylate, and other monomers occurs in the presence of beryllium chloride, lithium chloride, or metallic magnesium at the temperature of liquid nitrogen.

2. Formation of stereoregular polymers. An interesting feature of the polymers formed under these conditions is their regular spatial structure, in contrast to polymers obtained by radical polymerisation. Natta[11] explains this by the entry of monomer molecules between the catalyst surface and the end of the growing polymer chain, which grows like a tree, obtaining its supply analogously to roots from the soil, as shown in Fig. 1. Every monomer molecule which enters therefore arranges itself in the same way as all those which have entered previously, and the resulting polymer chain is made up solely of *dextro* or *laevo* units. Since at no instant during this process will the growing tip of the macromolecule be absolutely free, no racemisation will occur.

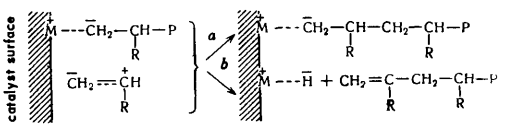


Fig. 1. Chain growth (*a*) and chain termination (*b*) during the formation of stereoregular polymers by ionic polymerisation.

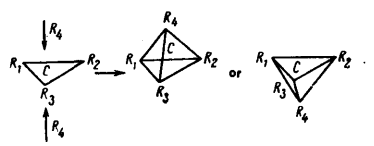


Fig. 2. Addition to a free radical.

In contrast to this, during radical polymerisation each of the similar carbon atoms remains for a short period of time in the state of a free radical. Addition of this free radical to the next olefin molecule can occur in two ways, as shown in Fig. 2. Since there are usually no reasons making one or other mode of addition more difficult, the

polymer formed has a random arrangement of atoms and atactic[32]. In some cases, however, formation of stereoregular polymers is possible even with radical polymerisation, if conditions are created which ensure that the monomer molecules shall be oriented, and which diminish their mobility (see below).

Every carbon atom in a polymer obtained by stereoregular polymerisation has a definite, recurring configuration. If all the asymmetric carbon atoms have the same configuration, an isotactic polymer is formed. If there is strict alternation of atoms having the *dextro* and the *laevo* configuration, a syndiotactic polymer is formed. Finally, if the distribution is random, as occurs with inactive catalysts, as well as during radical polymerisation, an atactic polymer will be obtained (see Fig. 21).

An interesting feature of isotactic polymers which has attracted attention to them is the fact that, because of the regular structure of the polymer chains, they are easily packed in the solid state and form crystalline products possessing high melting points and great strength (see Table 6). Natta[13] considers the presence of a solid catalyst surface to be an essential condition for the formation of isotactic polymers. No isotactic polypropylene is formed in the presence of the hydrocarbon-soluble catalyst system $Ti(OC_3H_7)_4 + Al(C_2H_5)_3$. When this catalyst is deposited on aluminium silicate ($SiO_2 + Al_2O_3$) 10% of isotactic polypropylene is obtained, and when it is deposited on $CoCl_2$, 35–45% results. This shows the necessity for the presence of a solid catalyst[13]. Three crystalline forms of $TiCl_3$ have been discovered, the α- (violet), β- (brown), and γ-forms[13]. The structure of the first two is shown in Fig. 3. The α-form gives the purest stereopolymers. With dienes the α- and γ-forms give *trans*-1,4- and the β-form yields *cis*-1,4-polymers.

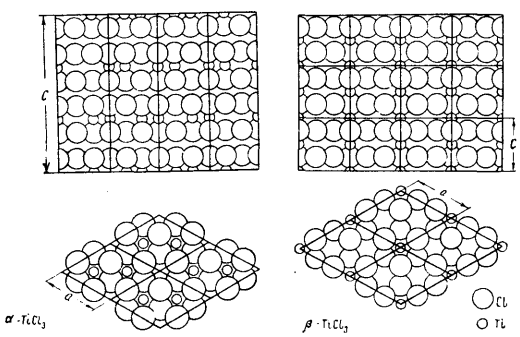


Fig. 3. Crystal structure of the α (violet) and β (brown) modifications of titanium trichloride.

Natta[13] has shown that the stereospecificity of a catalytic system depends also on the ionic radius of the metal in the metal alkyl: in the polymerisation of propene with $TiCl_3$ and a metal alkyl, the amount of isotactic polymer decreases with increase in the ionic radius: Be (r = 0.35 Å), 94–97%; Al (0.51 Å), 80–90%; Mg (0.66 Å), 78–85%; and Zn (0.74 Å), 30–40%.

Danusso and Sianesi[33] have shown that the stereospecificity of the $TiCl_4 + AlR_3$ catalyst system depends on the proportions of the components and is a maximum when $TiCl_4 : AlR_3 = 1 : 2.5$.

Very similar properties to those of polyethylene obtained with Ziegler catalysts are possessed also by polyethylene obtained at medium pressures (~ 50 atm) in the presence of a heterogeneous catalyst consisting of CrO_3 deposited on an aluminium silicate carrier ($SiO_2 + Al_2O_3$) (Phillips method)[34,35]. A continuous method for polymerising ethylene and propene at moderate pressures has now been worked out[36]. This process is particularly interesting when polyethylene is employed as solvent[37].

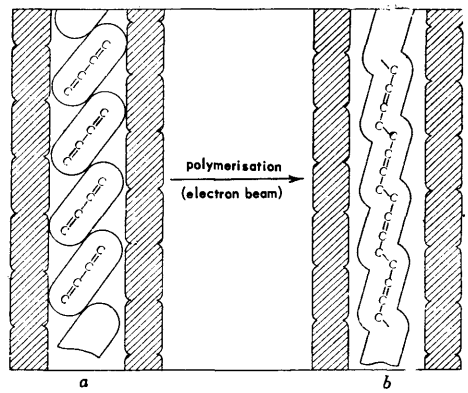


Fig. 4. Stereoregular polymerisation of butadiene in clathrate compounds under the influence of fast electrons: *a*) position of butadiene molecules before polymerisation; *b*) position after polymerisation.

Topchiev et al.[38] have investigated the structure and properties of molybdenum and chromium oxide catalysts, and have shown that with their aid polyethylene and polypropylene of a high degree of crystallinity can be prepared.

Recently stereoregular polymers have been successfully prepared with other catalysts. Thus Fridlander and Thomas[39] obtained crystalline polymers of α-methylstyrene and α,p-dimethylstyrene in the presence of boron fluoride, stannic chloride, etc. By polymerisation in the presence of a Grignard reagent, Muller et al.[40] obtained isotactic and syndiotactic polymers of methyl methacrylate, and Garrett et al. those of isopropyl acrylate[41]. Fox et al.[42] showed that at low temperatures (0°–75°) methyl methacrylate forms crystalline polymers even by radical polymerisation.

Browne and White[43] found that formation of crystalline polymers can occur as a result of the radical polymerisation of butadiene, acrylonitrile, vinyl chloride, vinylidene chloride, and cyclohexadiene by the action of a beam of electrons. The main condition for success is the use of clathrate compounds (inclusion compounds) of these monomers with urea. After completion of polymerisation the urea is removed. The monomer molecules occur in a definite position relative to one another, and this leads to the formation of stereoregular polymers. Butadiene under these conditions forms a crystalline *trans*-1,4-polybutadiene.

The clathrate compounds are crystalline solids containing channels filled with the monomer, the arrangement of the molecules being strictly fixed. On exposure to fast

electrons (1 MeV), therefore, addition of monomer molecules to one another occurs in a fixed position. For the same reason no branching occurs, since the chain can grow only by combination of the monomer head to tail, as shown in Fig. 4. The result is solid *trans*-1,4-polybutadiene. This process resembles stereospecific syntheses in living organisms.

Sakurada and Nambu[44] obtained a syndiotactic polymer of vinyl chloride by exposing the complex compound of the latter with urea to γ-rays (from Co^{60} of intensity 1000 c at 75° for 50–70 h).

3. Polymerisation by means of lithium alkyls. Organolithium compounds used with dienes enable the process to be carried out in such a way that the polymer formed contains up to 90% of structural units combined in the *cis*-1,4-position.

Korotkov et al.[45] investigated the polymerisation of isoprene, methyl methacrylate, and other monomers in the presence of butyllithium, and suggested the following mechanism for the process:

chain initiation:

$$RLi + M \rightarrow MRLi,$$

chain propagation:

$$M_iRLi + M \rightarrow M_{i+1}RLi,$$

chain termination by interaction of two growing chains:

$$M_iRLi + M_jR'Li \rightarrow R'M_iLi + RM_jLi,$$

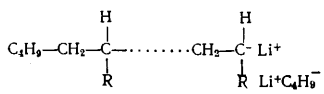
or by reaction with a catalyst molecule:

$$M_jRLi + R'Li \rightarrow R'M_jLi + RLi,$$

chain transfer:

$$M_iRLi + M \rightarrow RM_iH + MLi.$$

The structure of the transition state in this reaction is as follows[30]:



At the end of the chain is a quadrupole, which controls the addition of monomer to the growing chain.

Lithium alkyls in the presence of titanium tetrachloride form isotactic and amorphous polymers of olefins[15,23].

Fox et al.[46] found that polymerisation of methyl methacrylate in the presence of fluorenonelithium leads to the formation of stereoregular high polymers.

B. Preparation of Graft and Block Copolymers

A second new type of polymer is represented by the block and graft polymers and copolymers, whose structure had not been recognised although they have existed earlier. All polymers which have already been obtained for a long time by radical polymerisation are, owing to the occurrence of chain transfer, branched polymers, in which "grafted" side chains are attached to the main chain of the macromolecule. Fig. 5 shows diagrammatically an "ideal" linear polymer and a real polymer obtained by radical polymerisation. The presence of side chains has a great effect on the properties of the polymer, as numerous examples have shown recently. Branching exerts a particularly great influence on the ability to crystallise.

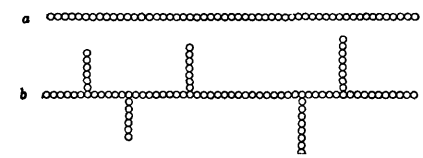


Fig. 5. Structure of (*a*) an "ideal" linear polymer and (*b*) a real polymer obtained by radical polymerisation.

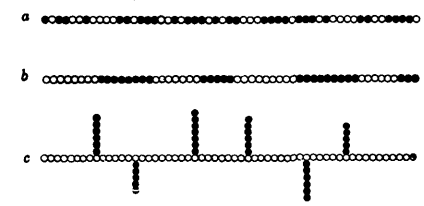


Fig. 6. Structure of "ideal" copolymers: *a*) normal, *b*) block, and *c*) graft copolymers.

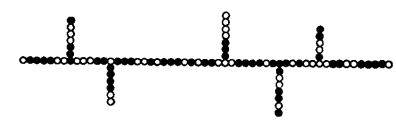


Fig. 7. Structure of a real copolymer obtained by a radical process.

The properties of the polymer are still more changed when the side chains in the graft copolymer are different in nature from the main chain. Such graft copolymers have been intensely investigated recently, and many methods are already known for obtaining them.

A block copolymer is a polymer whose macromolecule is made up of alternating fragments of polymers of different composition (blocks). The structure of graft and block copolymers is shown diagrammatically in Fig. 6. However, such a structure is possessed only by those copolymers, including block and graft copolymers, which are obtained by polycondensation or ionic polymerisation. Polymers obtained by radical processes have a different structure. They are characterised by the presence of a larger or smaller number of side branches of different size. This is shown diagrammatically in Fig. 7. In the same way, block copolymers obtained by a radical process possess a branched macromolecule, as shown diagrammatically in Fig. 8. This diagram shows quite clearly that the distinction between a block copolymer and a graft copolymer is extremely arbitrary. Graft copolymers are still more branched, as can be seen from Fig. 9.

A number of methods have been proposed for obtaining graft and block copolymers, based on processes of polycondensation and radical and ionic polymerisation, among

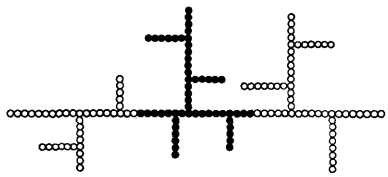


Fig. 8. Structure of a block copolymer obtained in a radical process.

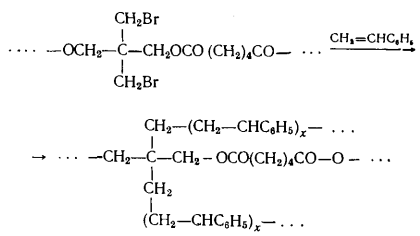
which are: (1) use of chain transfer; (2) method of active centres; (3) copolymerisation; (4) use of radiation; (5) preparation of block copolymers; and (6) a mechanical–chemical method. The results will be considered in the same order.

1. Use of chain transfer. Several procedures are available for preparing graft copolymers by this process: a polymer is added to a monomer undergoing polymerisation, and owing to chain transfer, fragments of the latter are grafted on to the polymer. Here formation of the graft copolymer is accompanied by that of a mixture of the two homopolymers[47,48].

Berlin was able to prepare graft copolymers by carrying out the polymerisation of vinyl chloride in a latex of a copolymer of butyl methacrylate with methacrylic acid[49], and also by the polymerisation of a mixture of butyl methacrylate and methacrylic acid in a latex of poly(vinyl chloride)[49]. He obtained a graft copolymer of butadiene–styrene rubber with polystyrene in this way[49].

The simplest case occurs when the reaction is carried out in a swollen polymer. Swift[50] observed that a monomer and an initiator within a swollen polymer form a graft copolymer (~ 25%) together with the homopolymer. Hartley[51] obtained a graft copolymer from vinyl acetate and polyvinyl alcohol by polymerising the former in a suspension stabilised with the latter.

In the polymerisation of styrene in the presence of the polyester of pentaerythritol dibromide and adipic acid Schonfeld and Waltcher obtained a graft copolymer[52]:



Here, more active points (bromine atoms) are produced, and this fixes the position of the grafts.

2. Copolymerisation. This is based on the use of polymers containing double bonds, at which the added monomer can enter into copolymerisation. This is usually accompanied by the formation of grafts by chain transfer. The relative proportions of these reactions depend on the structure of the polymer.

A widely used method for obtaining glass-like plastics reinforced with polyesters is based on the use as binders of polyesters of maleic, fumaric, or other unsaturated acid. These polyesters copolymerise with styrene or other monomers with formation of a graft copolymer. The formation of such copolymers has been studied in detail by Spasskii et al.[53] The introduction of groups having double bonds, e.g. by the formation of acrylic esters of cellulose followed by their copolymerisation with methacrylic esters, enables insoluble three-dimensional polymers to be obtained[49].

Merrett and Wood[48] modified natural rubber by forming graft copolymers with methyl methacrylate and styrene, and proved their formation by fractionation. Swift[50] impregnated rubber with the monomer and the initiator and then carried out the polymerisation, obtaining a graft copolymer together with a homopolymer.

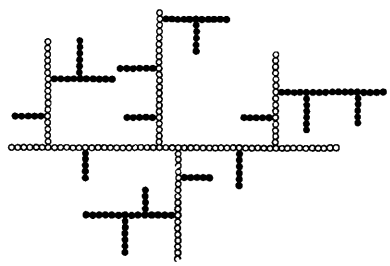
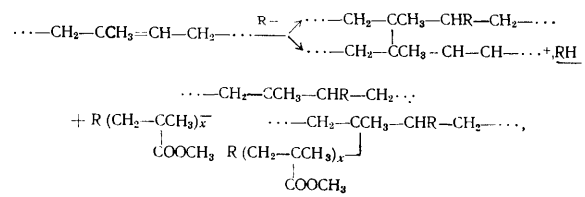


Fig. 9. Structure of a graft copolymer obtained in a radical process.

Kobryner and Banderet[54] investigated the reaction by which methyl methacrylate is grafted to natural rubber, and concluded that grafting is a result of combination of the growing poly(methyl methacrylate) chain with a free radical in the rubber chain:



where R = C_6H_5 or C_6H_5COO.

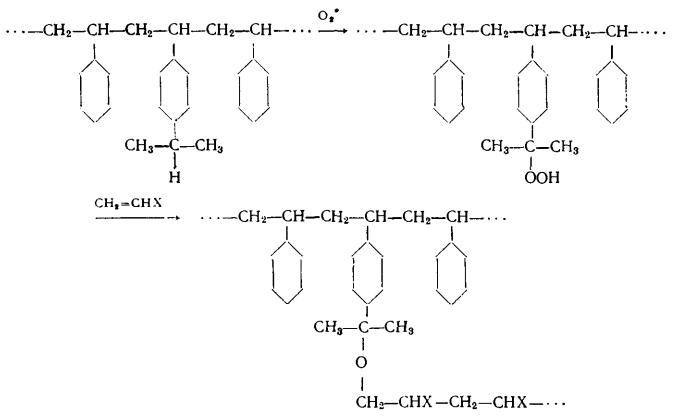
Thus grafting occurs partly by copolymerisation at the double bonds, and partly by chain transfer.

Abkin et al.[55] regard copolymerisation involving the double bond as unlikely, since from energy considerations chain grafting at a methylene group is more probable.

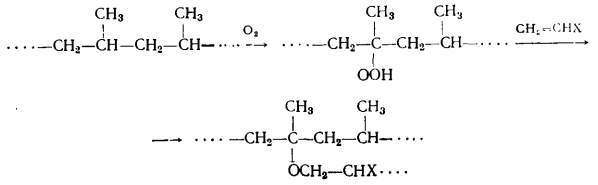
Banderet and Kobryner[56] broke down the graft copolymer of methyl methacrylate on natural rubber by the action of ozone, and isolated poly(methyl methacrylate) of molecular weight 350 000.

3. Method of active centres. A more reliable way of obtaining graft copolymers with a definite arrangement of the grafts is to form active centres in the original polymer, on to which monomer molecules are subsequently grafted. These active centres are formed in various ways.

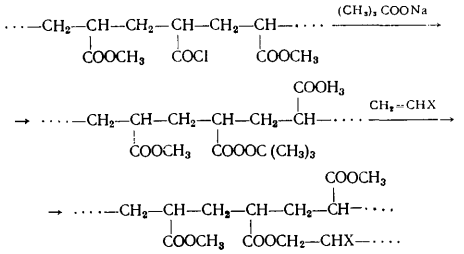
They can be obtained by oxidising such readily oxidisable groups as isopropyl, or by introducing peroxy groups by oxidation with ozone. In hydrolytic polymerisation other active groups are those containing reactive hydrogen atoms, etc. Mesrobian[57] introduced active groups by preliminary oxidation with atmospheric oxygen of a copolymer of styrene and *p*-isopropylstyrene. The resulting hydroperoxy groups form points at which monomer molecules are grafted on[57]:



Natta[58,59] used this method for grafting methyl methacrylate on to polypropylene and other isotactic polyolefins. When air is passed into a 15–20% solution of polypropylene, hydroperoxy groups are formed, on which monomer is then grafted:



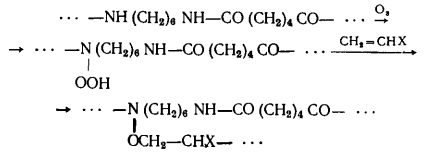
Smets et al.[59,60] prepared graft copolymers from a copolymer of methyl acrylate and acryloyl chloride by displacing the chlorine with t-butyl hydroperoxide:



Jones obtained a graft copolymer by ultra-violet irradiation of methyl methacrylate containing brominated styrene[61].

Manson and Cragg[62] employed oxidised polystyrene or a copolymer of styrene with 4-vinylcyclohexanone, copolymerising it with styrene.

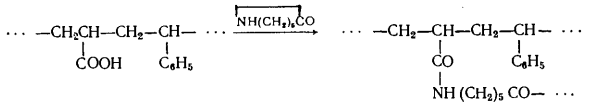
Korshak and Mozgova[63] found a way of obtaining graft copolymers by first subjecting the initial high polymers to the action of ozone to produce active hydroperoxy groups. The resulting polymer is then treated with a vinyl monomer, with the formation of grafts at the active groups. This method enables a graft to be made on any polymer. By means of it graft copolymers have been prepared of such polyamides as poly-ϵ-caprolactam (Capron, Perlon)[63,64], polyhexamethyleneadipamide (Anid, 6,6-nylon)[65], and the mixed polyamide Anid G-669[63,65,66], and also such polyesters as poly(ethylene terephthalate) (Lavsan, Terylene)[67], with monomers such as styrene, methyl methacrylate, acrylonitrile, and vinylidene chloride. The reaction probably occurs as follows:



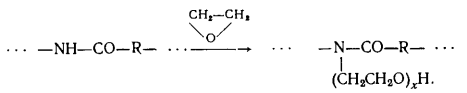
This method enables grafts to be made in the surface layer alone, making it possible to vary the surface properties of finished articles made of various high polymers. The ozonisation method proved to be suitable for other polymers as well, and was successfully employed by Kargin et al. for grafting styrene to starch[68] and also acrylonitrile or styrene to cellulose[69]. Kozlov et al.[70] prepared graft copolymers of polystyrene and acrylic acid in this way.

Wichterle and Gregor[71,72] suggested a method for grafting poly-ϵ-caprolactam on to the main chain of poly(methyl methacrylate). At first a copolymer of *N*-methacryloyl-ϵ-caprolactam with styrene is obtained, and then in ϵ-caprolactam medium, in the presence of alkali, side branches are grafted on, usually leading to the formation of a gel.

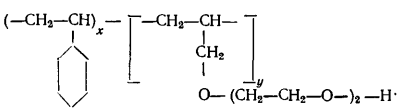
Chapman and Valentine[59,73] prepared graft copolymers of poly-ϵ-caprolactam on vinyl polymers containing COOH, $COOCH_3$, and NH_2 groups, e.g. the copolymer of styrene with methyl acrylate, acrylic acid, or maleic anhydride. The reaction is carried out in the presence of water:



Haas et al.[74] and Rafikov et al.[75] obtained graft copolymers by the action of ethylene oxide on polyamides:



Weiss et al.[76] synthesised graft copolymers of ethylene oxide on the copolymer of styrene with dimethyl maleate, and of styrene with allyl acetate, of the following structure:



4. Application of radiation. The use of high-energy or ultra-violet rays is an extremely promising method. The initial polymer, often containing halogen or similar atoms, is exposed to ultra-violet radiation or, better, to γ-rays from Co^{60}. Free radicals are formed at various points on the polymer by rupture of chains, splitting off of hydrogen, bromine atoms, etc., and grafting occurs at these points. Since the polymer is not changed uniformly by the action of the radiation, a complex product is formed, consisting of a mixture of graft and block copolymers together with a hybrid of them which is at the same time both a graft and a block copolymer. Fig. 10



Fig. 10. Structure of a graft block copolymer obtained by irradiation or by a mechanical method.

shows a diagram of such a graft block copolymer. The radiation method has been very widely employed by various investigators, in particular by Chapiro[77], Ballantine[78], and others[59].

Several methods are known for obtaining graft and block copolymers with the aid of ionising radiations[79]. The first consists in irradiating a mixture or a solution of two high polymers when the macroradicals which are formed combine to yield a block copolymer. However, the yield of the latter is small, since the formation of each macromolecule of graft copolymer is accompanied by two homopolymer molecules[79,80].

The second method consists in irradiation of a polymer in contact with a monomer, and also in solution or in emulsion[72]. A mixture of graft copolymer and homopolymer due to polymerisation of the monomer is formed[80-82]. Formation of homopolymer can be minimised by choice of appropriate starting materials or by reducing the amount of the original monomer taken. In the latter case some article made of the finished polymer is soaked in the monomer, and the swollen specimen exposed to the radiation[79,83,84].

In a third method the polymer alone is irradiated in air. The macroradicals formed react with atmospheric oxygen to form peroxy groups[83]. When the treated polymer is placed in the monomer, the peroxy groups form the active centres on which polymerisation of the monomer begins, leading to the formation of grafts[79,84]: any formation of homopolymer is insignificant. A given weight of the original polymer can have grafted on to it as much as 122 times its weight of a second polymer by this method.

Ballantine et al.[85] have shown that polymers can be irradiated in the absence of oxygen, and then the monomer added. The radicals which are formed initiate growth of the grafts.

Chapiro[86] grafted acrylonitrile on to polyethylene; above 135° a cross-linked copolymer is formed.

Cooper et al.[87] prepared graft copolymers of methyl methacrylate and natural rubber by exposing latex to visible light, ultra-violet radiation, and γ-rays.

5. Mechanical method. Mechanical processing of polymers (grinding, rolling, crushing, treatment with ultrasonic vibrations, freezing of a solution, etc.) is accompanied by destruction of the macromolecules with formation of macroradicals:

$$\cdots -CH_2-CHX-CH_2-CHX- \cdots \rightarrow \cdots -CH_2-CHX- + -CH_2-CHX- \cdots$$

If a mixture of several polymers is subjected to such treatment, recombination of the various macroradicals should yield block copolymers:

$$\cdots -CH_2-CHX- + -CH_2-CHY- \cdots \rightarrow \cdots -CH_2-CHX-CH_2-CHY- \cdots$$

block copolymer

The occurrence of chain transfer should, however, lead to the formation of branched graft copolymers and graft block copolymers (see section B. 4).

If mechanical destruction of a polymer is carried out in a monomer medium, the resulting macroradicals initiate polymerisation of the monomer, evidently with the formation mainly of a block copolymer together with a graft copolymer and a graft block copolymer (see section B. 4):

$$\cdots -CH_2-CHX- + CH_2=CHY \rightarrow \cdots -CH_2-CHX-CH_2-CHY- \cdots$$

$$\cdots -CH_2-CHX-CH_2-CHY- \cdots 2R \rightarrow \cdots -CH_2-\underset{|}{CX}-CH_2-\underset{|}{CY}- \cdots \xrightarrow{CH_2=CHY}$$

$$\rightarrow \cdots -CH_2-\underset{|}{\overset{|}{CX}}-CH_2-CY- \cdots$$

$$CH_2-CHY- \cdots \quad CH_2-CHY- \cdots$$

graft block copolymer

These two variants are employed in practice for the production of graft and block copolymers by mechanical means[88].

Angier and Watson[89] have shown that when natural rubber is cold-rolled together with chloroprene rubber, a graft copolymer is formed, the presence of which was proved by fractionating the product.

Dogadkin et al.[90], using a fractionation method, showed that when a mixture of natural and butadiene–styrene rubbers is masticated on microrollers, graft and block copolymers are formed.

Kargin[91] and other investigators used a mechanical method to obtain graft and block copolymers by plasticising a mixture of a phenol–formaldehyde resin with a copolymer of butadiene and acrylonitrile.

Berlin et al.[92] obtained a graft and a block copolymer by prolonged rolling of a mixture of poly(vinyl chloride) with phenol–formaldehyde resin.

Kovarskaya et al.[93] obtained graft and block copolymers of butadiene–acrylonitrile rubber with polystyrene and phenol–formaldehyde resin by a mechanical method from the finished polymers.

Slonimskii et al.[94] synthesised graft block copolymers of butadiene–styrene and sodium–butadiene rubbers with styrene or methyl methacrylate by subjecting the rubber mixed with the monomer to mechanical treatment. The resulting copolymers possessed better characteristics than the original rubbers.

Angier et al.[95] observed the formation of graft and block copolymers by the cold rolling of rubber with methyl methacrylate, methacrylic acid, chloroprene, and styrene, but vinyl chloride and vinyl acetate do not copolymerise with rubber under these conditions.

Angier et al.[96] prepared block copolymers by mechanical mixing of a polymer with a monomer, using twelve polymers and twelve monomers in different combinations. They investigated the reaction of such polymers as poly(methyl methacrylate), polystyrene, poly(vinyl acetate), poly(vinyl chloride), polyethylene, poly(vinylidene chloride), polyvinylpyrrolidone, a copolymer of styrene and butadiene (85 : 15), polyhexamethyleneadipamide (6,6-nylon), ethylcellulose, chlorinated rubber, and starch with the monomers methyl methacrylate, ethyl methacrylate, methacrylic acid, vinyl acetate, styrene, acrylonitrile, vinylpyrrolidone, vinylpyridine, vinylidene chloride, allyl acrylate, calcium acrylate, and divinylbenzene. It was found that copolymers were not formed in the case of vinyl acetate and polystyrene or poly(methyl methacrylate). In

the majority of the other cases formation of copolymer occurred after 20–30 min rolling.

Kargin and Plate[97] were able to graft monomers on to the surface of solid crystalline materials (quartz, common salt, and graphite) by grinding the latter in styrene or methyl methacrylate medium in a vibration mill.

Ultrasonic vibrations cause the destruction of polymers, so that exposure to them of a mixture of two polymers leads to the formation of block copolymers as a result of subsequent recombination, which has been shown in the case of a mixture of polystyrene and poly(methyl methacrylate)[98,99], as well as in other cases[100]. The action of ultrasonic vibrations on a solution of a polymer in a monomer leads to the formation of graft and block copolymers[101,102].

Berlin and his collaborators[103] have shown that disintegration of macromolecules with formation of macroradicals occurs when polymer solutions are frozen. If this is applied to starch in a vinyl-monomer medium, graft copolymers of starch with vinyl monomers are formed. A graft copolymer of starch with styrene has been obtained in this way.

6. Preparation of block copolymers. Both block and graft copolymers can be obtained by polycondensation as well as radical or ionic polymerisation. A block copolymer was obtained by Allen[104] by the polycondensation of dimethyl terephthalate with a mixture of ethylene glycol and poly(ethylene oxide). It contains blocks of poly(ethylene oxide) and poly(ethylene terephthalate), and can be represented as follows[105]:

$$\{[-O(CH_2CH_2O)_2COC_6H_4CO]_x(OCH_2CH_2)_y-\}_n.$$

An interesting method for obtaining block copolymers was proposed by Hicks and Melville[106]. They passed a monomer through a capillary tube illuminated with ultra-violet radiation. Polymerisation occurred, and the solution of the resulting polymer ran into a second polymer, which produced further growth in the active chains.

Orr and Williams[107] obtained a block copolymer of styrene with butadiene and other monomers. They first synthesised a block containing peroxy groups at the ends, by polymerisation of the appropriate monomer in the presence of *p*-diisopropylbenzene hydroperoxide. The resulting block was placed in styrene medium, when blocks of polystyrene grew on to its ends:

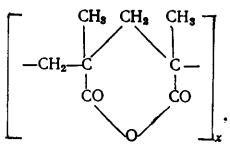
$$HOOROM_nOROOH \xrightarrow{CH_2=CHC_6H_5} (CH_2CHC_6H_5)_xOROM_nORO(CH_2CHC_6H_5)_y$$

Dunn et al.[108] employed for the production of block copolymers polystyrene prepared in the presence of carbon tetrabromide and containing CBr_3 groups at the ends of the macromolecules. This polystyrene was dissolved in methyl methacrylate and exposed to ultra-violet radiation, as a result of which the bromine atom was replaced by a growing chain, forming a block of methyl methacrylate units.

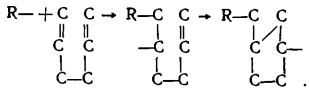
Bawn et al.[72,109] prepared block copolymers by the decomposition of aliphatic diazo compounds $RCHN_2$ under the influence of alkylborons. First of all one diazo compound was decomposed, and the first block was obtained with active end groups:

$$BX_2-(CH)_n-X;$$
$$\quad\quad\quad

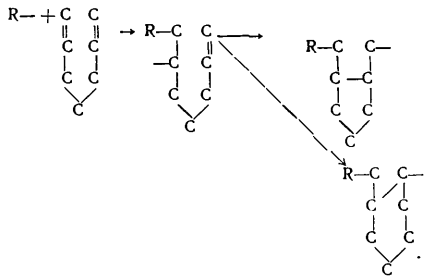
on radical polymerisation yields a polymer, which melts at about 200°, containing rings in the chain:



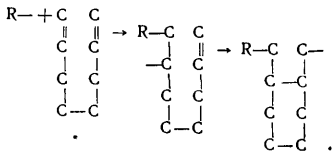
In general, cyclopolymerisation leads to the formation of five- or six-membered rings, the former being produced as follows:



Simultaneous formation of five- and six-membered rings can also occur:



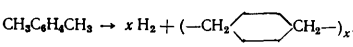
Six-membered rings are formed as follows:



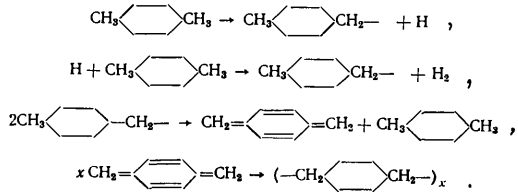
Thus the decisive factor is the number of atoms of carbon (or other elements) separating the double bonds. It varies between two and four. When the number of atoms is outside these limits, cyclopolymerisation obviously does not take place, and formation of linear or three-dimensional polymers will occur.

D. Dehydrogenation Polymerisation

Recently polymers containing aromatic nuclei in the chain have attracted a great deal of attention. Thus Szwarc[118] obtained a polymer of *p*-xylylene by pyrolysis of *p*-xylene vapour in a vacuum. The reaction leading to the formation of poly-*p*-xylylene is represented as follows:



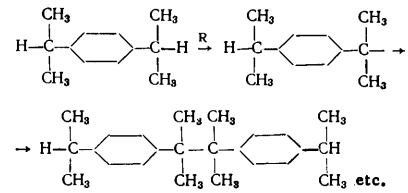
Errede and Landrum[119] showed that this reaction involves the intermediate formation of free radicals:



Rapid cooling and freezing of the products of the pyrolysis to -78° gave a solution of diradicals: these are evidently stabilised by the formation of a quinonoid structure. With iodine they form *p*-xylylene iodide, and when the solution is heated to 20° they polymerise, forming poly-*p*-xylylene.

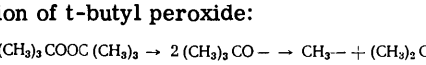
E. Polyrecombination

Korshak et al.[120-122] found a new way of obtaining compounds similar in structure to those described above, by polyrecombination. The initial hydrocarbon is treated with a peroxide. The secondary radicals formed combine with one another to form a polymer chain, as shown by the following equation:



Thus *p*-diisopropylbenzene yields a polymer by stepwise polyrecombination.

The initial primary radicals can be obtained by the decomposition of t-butyl peroxide:



This is usually accompanied by the formation of both butoxy and methyl radicals, their proportions depending on the temperature and the properties of the solvent. The molecular weight of the polymer depends on the amount of peroxide taken, as shown in Fig. 11. During the reaction there is a gradual conversion of monomer to polymer by a stepwise mechanism. Fig. 12 shows the variation in the composition of the reaction mixture as a function of the amount of peroxide taken.

F. Radical Polymerisation

At the present time radical polymerisation is the main method of preparing the most important polymers. The great scientific and practical achievements of this branch of the chemistry of high polymers have been described in a number of monographs[123,124] and reviews[125,126], and therefore they will not be discussed here.

G. Polycondensation

The results of numerous investigations on polycondensation have been reviewed in monographs[127,128]. Together with the broad development of research on classical lines, aimed at studying the mechanism and the kinetics of polycondensation, a new approach consists in carrying out the reaction at the boundary separating two phases[129-132].

The starting materials are an acid chloride of a dicarboxylic acid dissolved in benzene, carbon tetrachloride, chloroform, etc. and a diamine, diphenol, etc. dissolved in water as the second component. The reaction is represented by the equation



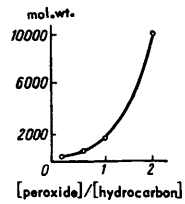


Fig. 11. Variation of molecular weight of polymer of *p*-diisopropylbenzene with molar ratio of peroxide to *p*-diisopropylbenzene.

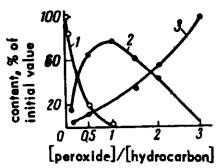


Fig. 12. Composition of reaction products of polyrecombination as a function of the amount of peroxide added: 1) diisopropylbenzene; 2) polymers of low molecular weight; 3) polymers of high molecular weight.

Alkali is added to the aqueous layer to neutralise the acid which is formed. A film of polyamide is produced at the boundary between the two phases. If the initial solutions are mixed rapidly, a fine powder is obtained. The reaction product can also be obtained in the form of a fibre.

Morgan[129] points out that polymer formation occurs in the organic phase, to which the diamine diffuses. The role of the aqueous phase is a solvent for the diamine or the diphenol, an acid acceptor, and a medium which serves to remove the acid formed. The laws governing polycondensation at the boundary between two phases differ from those for ordinary polycondensation in that the process is non-equilibrium in character, excess of the starting materials has no effect on the molecular weight of the resulting polymer, etc.[130]

Korshak et al.[130] have found that the molecular weight of the polyamide does depend on the concentration of the reactants, as shown in Fig. 13. It is not affected by the relative proportions of the starting materials (see Fig. 14). For comparison this diagram shows also a curve demonstrating the variation in molecular weight with the relative proportions of the starting materials for equilibrium polycondensation. In addition, the molecular weight is strongly affected by the presence of such monofunctional substances as monoamines and chlorides of monocarboxylic acids, as shown in Figs. 15 and 16.

Korshak et al.[133] have investigated the reaction of dichlorides of aromatic dicarboxylic acids with diphenols, and have shown that in this case there is an optimum concentration of the reactants at which the resulting "polyarenate" has the maximum molecular weight.

In a two-phase system polycondensation is carried out at comparatively low temperatures, and can yield products of very high molecular weight with a non-equilibrium distribution[30]. Polyamides and polyurethanes can be obtained with very high melting points: such polymers are impossible to obtain in the usual way owing to their decomposition at the high temperatures required by normal polycondensation.

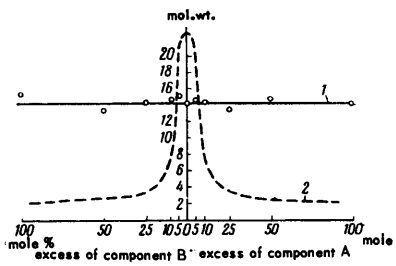


Fig. 14. Dependence of molecular weight of polyamide on the presence of an excess of starting materials: 1) during two-phase (non-equilibrium) polycondensation with excess of hexamethylenediamine (A) and of adipoyl chloride (B); 2) as above, during equilibrium polycondensation.

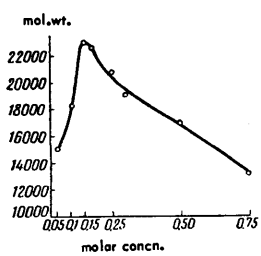


Fig. 13. Variation of molecular weight of polyamide with initial concentrations of reactants.

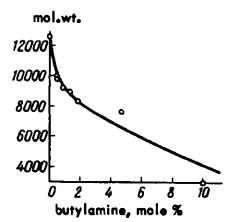


Fig. 15. Change in molecular weight of polyamide with amount of butylamine added.

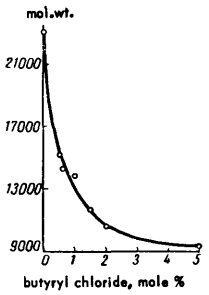


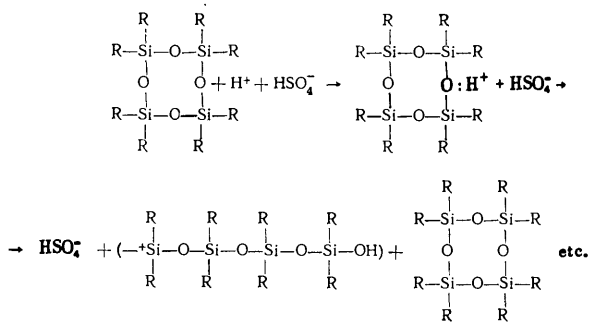
Fig. 16. Variation of molecular weight of polyamide with amount of butyryl chloride added.

H. Polymerisation of Cyclic Compounds

Great advances have been made in the polymerisation of cyclic compounds. A great deal of research has been devoted especially to the polymerisation of ϵ-caprolactam[134]. Wichterle[135] developed a method for the rapid polymerisation of ϵ-caprolactam in the presence of alkaline reagents, which enables this process to be carried out in a few minutes instead of the many hours required for polymerisation in the presence of water.

Mention must be made of the reversible polymerisation of the six-membered carbonates of $\epsilon,\epsilon,\epsilon'$-disubstituted 1,3-propanediol, studied by Sarel and Pohoryles[136].

The polymerisation of cyclic siloxanes in the presence of sulphuric acid and other catalysts, leading to the formation of linear macromolecular polysiloxanes, has attracted a great deal of interest[137-140]. Andrianov and Yakushkina[137] suggest the following reaction mechanism:



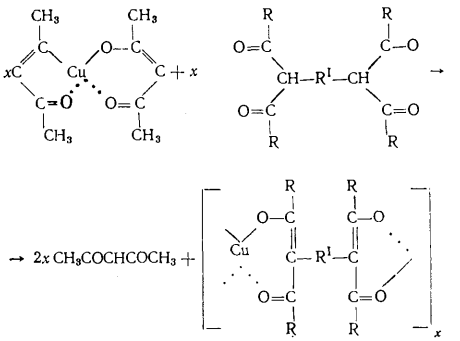
J. Preparation of Polymers by Complex Formation

A new way of preparing polymers of previously unknown type consists in using the reaction of complex formation to build up a polymer chain[133,140-143]. Reaction is carried out between a complex containing several complex-forming groups and metal ions or such relatively simple complexes as metal acetylacetonates. Chelate structures are formed, consisting of complex heterocycles with the central metal atom, which are far more stable than ordinary complexes. This effect of an increase in stability accompanying the formation of chelate compounds is explained by an increase in entropy of such complexes in comparison with the original substances.

In the preparation of complex polymers, the acceptors generally employed are cations of the transition metals — V^{3+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, Ag^{+}, Pt^{2+}, etc. — or the ions Ga^{3+}, In^{3+}, Te^{3+}, Ce^{4+}, and Pb^{2+}, which follow them. The small sizes of these cations in combination with their high effective charge, as well as the presence in some cases of unfilled *d* orbitals, ensure a stable bond with donor groups. Ions of the alkaline-earth metals and the lanthanides are feeble acceptors, and alkali-metal ions form complexes only in rare cases.

Complexones which are to be used to obtain chelate polymers should contain in their molecule such donor groups as $-NH_2$, =NH, =N, =NOH, –OH, =CO, –COO–, $-PO(OH)O-$, $-SO_2O-$, –S–, =C=S, etc.

A typical example of the formation of a complex polymer is the reaction between tetraketones and a metal acetylacetonate[140,142,143]:



For individual representatives see part III, section B. 11.

III. NEW HIGH POLYMERS

Many new polymers have been obtained both by using new methods of synthesis and by applying those which are already known. In view of their immense number, any complete description of all these polymers within a short review is impossible, and we must confine ourselves to isolated examples, which will serve as an illustration of the most important achievements in synthesis and as an indication of the main trends in the development of this field.

We must first note the tendency during recent years to develop production and research work on polymers based on petroleum chemicals, coal, and natural gas, which represent the most readily available and cheapest forms of raw materials for the large-scale production of a great number of polymers. This trend is shown by the production of polyethylene, isotactic polypropylene and other stereoregular polymers of α-olefins, polyformaldehyde, polyacrylonitrile, polystyrene, polybutadiene, polyisoprene, and other polymers which form the starting materials for the production of plastics, synthetic fibres, and synthetic rubber. The bulk production of cheap polymers has the aim of satisfying the day-to-day needs of industry and the demands of the population for various types of consumer goods.

There is also a marked tendency to seek polymers of higher quality than those already known, which are required to satisfy the needs of modern technology, demanding high thermal stability, great chemical stability, and high mechanical strength, electrically insulating or semiconducting properties, etc.[144]

Nesmeyanov[145] points out that a solution of this problem is to use different elements for the synthesis of polymers and so to bring into this field all the remaining elements of the Periodic System. This trend is reflected in the

development of organosilicon polymers and analogous polymers containing other elements.

In addition to these lines of development, great progress has been made in the synthesis and processing of polymeric materials and in the search for new fields of application for already known substances. As a result, more and more new articles are appearing, based on polymers which have already been known for a long time.

An example is the use of monomers of very high purity, yielding high polymers which are very stable to the action of elevated temperatures, light, etc.[146] Application of this method to poly(vinyl chloride) give a polymer which can be worked without the use of plasticisers. Thus in this case, although we are dealing with a polymeric material which has long been familiar to us, improvement in the technology of its production has actually provided us with a completely new product.

The position is similar with block copolymers and graft copolymers, which include units of known monomers, but with a different arrangement from that in the usual, irregular copolymers. The properties also change, resembling those of a mixture of polymers rather than a normal copolymer.

Grafting a layer of one polymer on to the surface of another is a new method of modifying the surface properties of polymers, enabling such characteristics as adhesion, dyeing properties, and stability to light, chemical reagents, etc. to be varied, and providing us with a polymer having a different combination of properties.

Individual high polymers will now be considered, dividing them into separate groups in accordance with the previously suggested chemical classification of high polymers based on the structure of the main chain and the nature and number of the substituents[147].

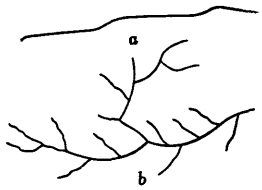


Fig. 17. Structure of the macromolecule of (*a*) low-pressure and (*b*) high-pressure polyethylene.

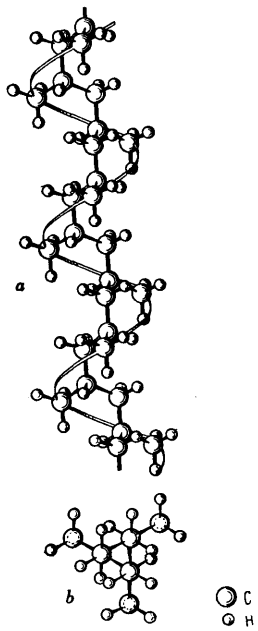


Fig. 18. Conformation of the macromolecule of isotactic polypropylene: *a*) side view; *b*) view from above.

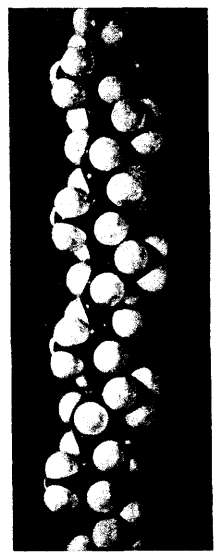


Fig. 19. External view of a model of the macromolecule of isotactic polypropylene.

A. Carbon-Chain Compounds

1. Saturated polyhydrocarbons (polyethylene and its homologues). Representatives of this first group of saturated carbon-chain high polymers which have been known for a long time are polyethylene, polyisobutylene, and polystyrene. Recently, after the work of Ziegler and Natta[7,10] in discovering new methods for polymerising olefins, this group has been expanded by a number of new compounds. Great advances have been made by the Soviet scientists Topchiev, Krentsel', and others in the development of methods for polymerising ethylene and other olefins[8,24,35].

The monomers are readily obtained from petroleum and these polymers are becoming increasingly important. Among them low-pressure polyethylene must be mentioned first. It is distinguished from the previously known high-pressure polyethylene by an almost complete absence of branching and a high molecular weight. Fig. 17 shows diagrammatically the molecules of the two types of polyethylene.

Low-pressure polyethylene has already acquired considerable importance. Its preparation by the Ziegler method[48] is based on the use of organoaluminium compounds containing added titanium tetrachloride as polymerisation catalysts. Polymers obtained with these catalysts have no chain branching, which affects their physical properties. Thus the usual branched, high-pressure polyethylene melts at 107°–120°, whereas the unbranched polymer obtained at low pressures by the Ziegler method melts at 130°–138°. Low-pressure polypropylene melts at 165°–175°, whereas propene yields only liquid polymers of low molecular weight on radical polymerisation.

Recently the production of polyethylene by the Phillips method based on the use of solid catalysts (Al_2O_3 + SiO_2 + + CrO_3) under moderate pressure[34,38,149] (50 atm) has successfully competed with the Ziegler method. We may note also a method based on the use of very high pressures (5000–20 000 atm)[150,151].

A new method for the polymerisation of ethylene by exposure to γ-rays[152,153] can yield a highly crystalline polyethylene resembling the product obtained at low pressures. Table 4 gives several properties of polyethylenes obtained in various ways. The applications of polyethylene are extremely varied, and are discussed in a number of papers and reviews[20,22,154].

A very promising new polymer among the polyolefins is isotactic polypropylene. Topchiev and Krentsel' et al.[155,156]

TABLE 4. Properties of polyethylene obtained by various processes.

Polythene specimen	M.p., °C	Density, g/cm³	Tensile strength, kg/cm²	Relative elongation at rupture, %	Amorphous content, %	Ratio of side chains to number of carbon atoms in main chain
High pressure	105	0.92	110—140	150—600	36—45	1 : 46
Low pressure	130	0.96	200—300	112—1000	7—13	1 : 333
Moderate pressure	127	0.97	200—400	400	7—10	1 : 667
Very high pressure	127	0.96	200—400	1200	10	1 : 200

have investigated the polymerisation of propene using an organometallic catalyst, and have shown that a good polymer can be obtained even from technical propene.

Polypropylene has a low specific gravity and a high melting point[157]. It melts at 160°–170° and has a specific gravity varying between 0.842 and 0.914, depending on its crystallinity. Isotactic polypropylene has a spiral arrangement of the side groups[158], as shown in Fig. 18.

Fig. 19 shows an external view of a model of a polypropylene macromolecule[158]. This polymer has been suggested as a starting material for a synthetic fibre. The polypropylene fibre is characterised by high strength, which is not inferior to that of other synthetic fibres[158], as is shown in Fig. 20.

Pipes can be made from polypropylene which can operate up to a temperature of 100°. Their strength is considerably greater than those of polyethylene[159]. Polypropylene is known in Italy under the name Moplen, in the USA as Pro-Fax, and in Western Germany as Hostalen.

The properties of polymers obtained from homologues of ethylene by polymerisation with Ziegler catalysts are set out in Table 5, which shows that the majority of the high polymers have high melting points and are crystalline materials of great mechanical strength, so that they will undoubtedly find wide application in industry.

Apart from isotactic polypropylene, other isotactic polymers have been prepared and are characterised by higher melting points than the corresponding atactic polymers[20]. At the present time isotactic polymers of

TABLE 6.

Polymer	M.p., °C	
	isotactic	atactic
Polypropylene	170	80
Polystyrene	220	80
Poly(methyl methacrylate)	200	115

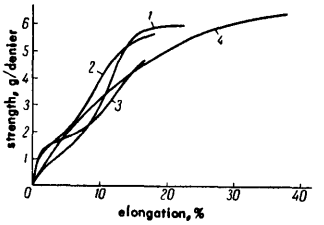


Fig. 20. Load—elongation curves for various synthetic fibres: 1) nylon; 2) Dacron; 3) Orlon; 4) polypropylene.

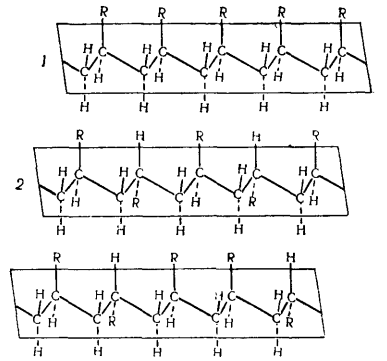


Fig. 21. Plane diagram of the chain structure of polymers of α-olefins: 1) isotactic; 2) syndiotactic; 3) atactic. The broken lines link atoms and groups situated below the plane.

TABLE 5. Properties of some polymeric hydrocarbons[8,160].

Polymer	Structural unit	M.p., °C	Density, g/cm³
Polypentylene	$-CH_2-CH_2-$	130—138	0.95—0.96
Polypropylene	$-CH_2-CH(CH_3)-$	165—175	0.90—0.92
Poly-α-butylene	$-CH_2-CH(CH_2CH_3)-$	126—128	0.91—0.92
Polyethylene	$-CH_2-CH((CH_2)_2CH_3)-$	75—80	0.87
Poly(3-methylpent-1-ene)	$-CH_2-CH(C_4H_9)-$	245—300	0.90
Poly(4-methylhex-1-ene)	$-CH_2-CH(C_5H_{11})-$	188	—

styrene[161], methyl methacrylate[42], vinyl chloride[43], and others[43] have been obtained.

An interesting feature of stereoregular polymerisation occurring in the presence of alkylaluminium catalysts is, as already noted (part II, section A 2), the possibility of obtaining three types of high polymers, differing in their conformation (isotactic, syndiotactic, and atactic). Fig. 21 shows the structures of these three types of polymers and the distinction between them. Table 6 gives for comparison the properties of isotactic and atactic polymers.

Isotactic polymers represent a new class of polymeric compounds of very great practical interest, since they are distinguished by high thermal stability and great mechanical strength compared with the corresponding atactic polymers[8,20]. This is explained by the fact that stereoregular polymers easily pack together owing to the regular arrange-

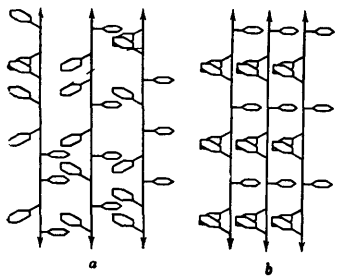


Fig. 22. Relative positions of side groups under conditions of close packing in (*a*) atactic (irregular) polystyrene and (*b*) isotactic polystyrene.

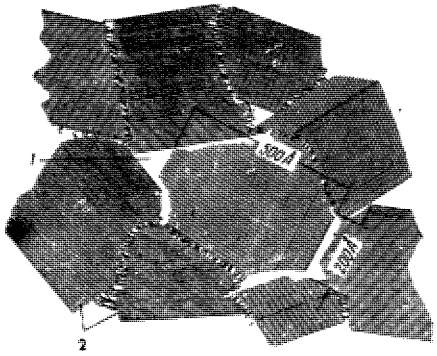


Fig. 23. Structure of a crystalline polymer: 1) amorphous regions; 2) crystalline regions.

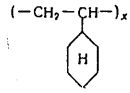
ment of side groups, in contrast to atactic polymers, in which the side groups prevent close packing of the macromolecules, as is shown in Fig. 22.

The regular structure of the chain facilitates crystallisation of the polymer, so that a large proportion of the macromolecules are contained in the crystalline phase, whereas the amorphous phase, filling the interstices between the crystals, is small. Fig. 23 shows the structure of the crystalline polymer.

Natta et al.[162,163] have reported the preparation of stereoblock polymers of propene, the molecules of which contain both isotactic and atactic blocks. Such polymers melt over a wider temperature range (100°–170°) and possess a greater elongation (100–200%) and a lower modulus of elasticity than isotactic polymers (Fig. 24). Mikhailov et al.[164] isolated stereoblock polymers of propene by extraction with heptane, and showed that such a structure is specific to polymers obtained by stereoregular polymerisation.

Copolymers of ethylene and propene obtained by Natta proved to be of great interest, since they possess elastic properties and yield very good and cheap rubbers, known as "C23" (Italy). They have the same elasticity as natural rubber, high tensile strength, and high relative elongation[165]. They are also very stable to the action of ozone and other oxidising agents.

A very interesting isotactic polymer is that of vinylcyclohexane (m.p. 300°):



A promising field for the application of isotactic polymers and polyethylene is the manufacture of synthetic fibres. These fibres are characterised by great strength in both wet and dry states[160].

Such a long familiar high polymer as polystyrene, which is manufactured in large quantities, is characterised by the desirable properties of transparency, good electrical insulation, etc., but has the great disadvantage of being inherently brittle owing to its low impact strength. This defect can be eliminated by copolymerising styrene with other monomers, and because of this, a number of copolymers of styrene are in practical use. Among them must be mentioned copolymers of styrene with acrylonitrile, methacrylonitrile, and methyl methacrylate containing 15–20% of one of these monomers, and also the ternary copolymer of styrene with acrylonitrile and butadiene.

The ternary copolymer, known as Kralastic[167], possesses good impact strength, increased hardness, high strength, and stability to the action of chemical reagents, and is used for the manufacture of pipes, fittings, etc.[166] Pipes made of Kralastic can be used to transport hot water and steam at moderate pressures[168].

The ternary acrylonitrile–butadiene–styrene copolymer was chosen to replace brass in the manufacture of shell cases. Its density is half that of brass and it showed good results at pressures of 420–2450 kg/cm² and with a flame lasting for a minute at a temperature exceeding 2200°.[160]

The copolymer of styrene with methyl methacrylate (Perlon 150) is a thermoplastic material possessing high

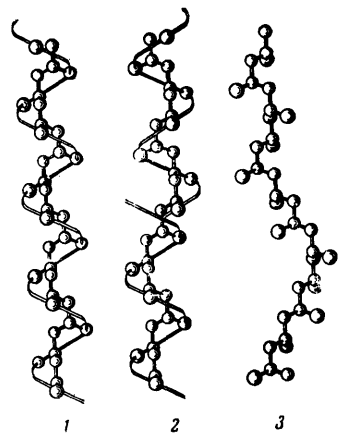


Fig. 24. Three-dimensional structure of the macromolecule of (1) isotactic polymer, (2) polymer with alternating isotactic and syndiotactic units, and (3) atactic polymer.

transparency, good strength, and resistance to heat and light[170]. The copolymer of styrene with acrylonitrile (polystyrene 51 or styrene 767) possesses greater hardness, impact strength, wear resistance, and stability to the action of solvents[171,172]. These copolymers are characterised by considerably greater strength and lower brittleness, and have an impact strength five times as great as that of ordinary polystyrene.

The polyhydrocarbon obtained by heating poly(vinyl acetate) or treating poly(vinyl alcohol) with concentrated sulphuric acid possesses interesting semiconducting properties. The product thus formed can be termed "polymethine" or "polyvinylene" in conformity with its structure[173]:

$$(-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-)_n \xrightarrow{-nH_2O} (-CH=CH-)_n$$

It is used for the manufacture of polarising sheets, and withstands heating to 600°.

2. Halogenated polyethylene derivatives. Apart from such widely and long familiar representatives of this group as poly(vinyl chloride), poly(vinylidene chloride), polytetrafluoroethylene, and polytrifluoroethylene, a number of new compounds of this type have recently been prepared, and the former compounds have found a number of new fields of application. New types of fibres have evolved, based on poly(vinyl chloride) — Teviron (Japan) — and on poly(vinylidene chloride) — Saran (USA).

Chlorinated poly(vinyl chloride), sometimes incorrectly termed "perchlorovinyl", has been used for the manufacture of the synthetic fibres Chlorin, Acetochlorin, and Vinitron[174,175]. Acetochlorin is obtained from a mixture of chlorinated poly(vinyl chloride) and cellulose acetate (15%), and Vinitron from a mixture with cellulose nitrate (30%)[174].

Among chloro derivatives of polyhydrocarbons must be mentioned also chlorinated polyethylene (sometimes incorrectly termed "perchloroethylene") and chlorosulphonated polyethylene. The former, depending on the method of chlorination, is a product melting at temperatures between 40° and 90°. Like poly(vinyl chloride), it is used for the manufacture of electrical insulating materials and other purposes. Chlorosulphonated polyethylene is obtained by treating polyethylene with a mixture of chlorine and sulphur dioxide. The best properties are displaced by a product containing 27% of chlorine and 1.5% of sulphur, in which one chlorosulphonyl group is present for every ninety carbon atoms, and one chlorine atom for every seven carbon atoms. This is a rubber-like material which can be vulcanised, and is termed Hypalon: it is used for the manufacture of rubber compositions, various coatings, etc.[8]

Krentsel' et al.[176] prepared chlorinated and chlorosulphonated polypropylene, which are of great interest as new polymeric materials.

Other representatives of this group of polymers are the fluoro derivatives, which represent the most thermostable group of organic polymers. The most important polymer of this type is polytetrafluoroethylene (Teflon), which has long been used as a heat-resistant material, very stable to chemical corrosion, owing to which it has gained the descriptive name of "the organic platinum". The production of polytetrafluoroethylene in the USA amounts to 2000 tons annually[177]. Recently it has acquired a new field of application in the textile industry for the manufacture of a synthetic fibre[178]. This fibre and cloth made from it are characterised by great chemical and thermal stability. Teflon (Fluoroplast) is used for the manufacture of films employed for the magnetic recording of sound and vision[179].

The new material Duroid is a ceramic fibre (50% silica and 50% alumina) which is coated with polytetrafluoroethylene and then formed into homogeneous sheets. This material has been used as packing where polytetrafluoroethylene itself cannot be used because of high pressures, e.g. in the flanges of pipelines[180].

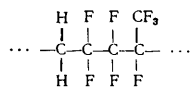
Rogovin has described a fibre, Ftorlon, which is characterised by high thermal stability. It is prepared from a copolymer of acrylonitrile and vinylidene fluoride[181,182].

A copolymer of tetrafluoroethylene and hexafluoropropylene (Teflon 100X) is more easily worked than polytetrafluoroethylene[183], can be pressed into sheets at 300°–350° without appreciable decomposition, has a high elasticity, and is transparent in relatively thick layers[184]. It is used to make tubes, films, vessels, and other articles. It softens at 285° and can be used at temperatures between -185° and +203°.

Polychlorotrifluoroethylene[177] is also widely employed.

Several new polymeric fluorides have appeared recently. Poly(vinyl fluoride) $[-CH_2-CHF-]_x$ (Polymer E) is a new polymer characterised by high thermal stability. It melts above 200° and, in view of its great strength and comparative accessibility, will obviously find wide application[177,182]. Poly(vinyl fluoride) film, which is distinguished by great resistance to the action of acids, alkalis, and solvents, is now made[185]. This film can be employed at temperatures between -100° and +200°. Its dielectric constant is 7.5. It is stronger than Mylar[182].

Fluoro rubbers based on copolymers of fluorinated ethylenes have been greatly developed. A very heat-resistant rubber is a copolymer of vinylidene fluoride and hexafluoropropylene (Viton A)[186,187]:

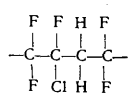


Its softening temperature is ~300°.[182]

A characteristic feature of Viton A is its high thermal stability[177]. Articles made of it withstand prolonged heating in dry air at 315°, and in oil and other solvents at 200°. Viton A can be worked on ordinary equipment[188]. Table 7 shows the temperature and time of ageing, in a thermostat with air circulation, during which the elastic properties of the vulcanised rubber are fully maintained (elongation not less than 100%)[188].

Viton A retains its elasticity down to -70°.[182] It is used for making diaphragms in pumps for gases, air conduits for the transfer of hot air, and hose for pumping hot liquids. Mixed with epoxy resins it is used for bonding ceramics to produce a material applicable at high temperatures. Viton A can be vulcanised with amines or peroxides, and also by means of high-energy radiation.

Another interesting copolymer is that of chlorotrifluoroethylene and vinylidene fluoride:



It is a rubber known as Kel-F. It is stable above 300°. It

has high strength and abrasion resistance, and is stable to the action of oils, fuels, and nitric acid; it is swollen by ethers[186].

A copolymer of vinyl fluoride and hexafluoropropylene also possesses the properties of an extremely heat-resistant rubber[189].

New polymers of perfluoroalkyl propenyl ketones[190], perfluoroalkylacrylamides[191], and pentafluorostyrene[192] have been described.

3. Oxygen derivatives of polyethylene. Poly(vinyl alcohol), which has been known for a long time, has found a new field of application in the manufacture of a synthetic fibre, known as Kuralon (Japan) or vinylon (USSR and USA). Ushakov developed a process for obtaining vinylon fibre from poly(vinyl alcohol)[193]. This fibre is distinguished by outstanding tensile strength and a markedly hydrophilic nature. Ushakov[194] has prepared copolymers of vinyl acetate with crotonamide and with hydroxymethylcrotonamide, which on heating readily give three-dimensional cross-links, of interest for the production of a synthetic fibre of increased strength and for other purposes.

Several new compounds have been obtained belonging to the group of acrylic polymers, among which the isotactic and syndiotactic acrylate polymers must be mentioned first. Fox et al.[48] prepared stereoregular polymers of methyl methacrylate in the presence of fluorenonelithium in the solution. Their glass and melting points are given in Table 8.

TABLE 7.

Temperature, °C	Time, h
200	2400
228	1000
255	250
282	72
310	24

TABLE 8. Melting points and glass points of stereoregular polymers of methyl methacrylate.

Type of polymer	Glass point, °C	Melting point, °C
Isotactic	115	200
Syndiotactic	45	160
Stereoblock	60—95	170

Isotactic poly(isopropyl acrylate)[41] is a crystalline substance melting at 162°.

Apart from the long familiar polymeric esters of acrylic and methacrylic acids, many new polymers and copolymers of this series have now appeared: e.g. such compounds as polymeric esters of acrylic and methacrylic acids and various fluorinated monohydric alcohols. These polymers possess elastic properties and great chemical stability, since the main polymer chain is surrounded by quite long fluorinated groups which protect it from external attack. One which has found practical application is poly(heptafluorobutyl acrylate) (Fluoro-rubber F4):

$$(-CH_2-CH-)_x$$
$$\quad\quad|$$
$$\quad COOCH_2(CF_2)_2CF_3.$$

It is stable up to 300° and possesses high strength, thermal stability, and resistance to benzene and oils[177].

Another interesting product is poly(trifluoromethoxyhexafluoropropyl acrylate) (Fluoro-rubber EF4)[177]:

$$(-CH_2-CH-)_x$$
$$\quad\quad|$$
$$\quad COOCH_2CF_2CF_2OCF_3.$$

It has better characteristics at low temperatures than the previous rubber[186].

4. Nitrogen derivatives of polyethylene. Interesting properties are possessed by polymeric esters of α-cyanoacrylic acid:

$$\left(\begin{array}{c} CN \\ | \\ -CH_2-C- \\ | \\ COOR \end{array}\right)_x.$$

They have found application as adhesives, which stick various materials very firmly together. The β-methoxyethyl and β-ethoxyethyl esters are recommended for this purpose. These glues contain no solvent, and set rapidly at ordinary temperatures directly in the glued joint[195]. Vinylidene cyanide $CH_2=C(CN)_2$ has been applied in the form of a copolymer with vinyl acetate for the manufacture of a synthetic fibre, Darvan[196].

Finally, polyacrylonitrile has increasing application in the manufacture of the synthetic fibres Orlon and Nitron or Zefran[197], which are valuable substitutes for wool. A fibre can be obtained also from polymethacrylonitrile[198].

Several copolymers of acrylic derivatives find application in the manufacture of synthetic fibres. Thus it is proposed to make a fibre from a copolymer of acrylonitrile and methyl acrylate (Creslan or Courtelle fibre)[199], from a copolymer of acrylonitrile and vinyl acetate (Verel fibre)[200], and from a copolymer of acrylonitrile with vinylidene chloride (Verel or Saniv fibre)[200,201]. A copolymer of acrylonitrile with methacrylamide (5–10%) gives a strong fibre with good dyeing properties[202].

Polymers of *N*-carboxyphenylmethacrylamides synthesised by Koton[203], are new derivatives of methacrylic acid, with high glass temperatures (~200°):

$$\left[\begin{array}{c} CH_3 \\ | \\ -CH_2-C- \\ | \\ CO \\ | \\ NH \\ | \\ \text{C}_6\text{H}_4 \\ | \\ COOH \end{array}\right]_x$$

5. Unsaturated polyhydrocarbons. Considerable progress has been made in the group of polymers of diene compounds, the majority of which are rubber-like materials. Apart from natural rubber, this group was previously represented by polybutadiene (sodium–butadiene rubber), polychloroprene, and also copolymers of butadiene with styrene or acrylonitrile.

Polymers of isoprene $[-CH_2-C(CH_3)=CH-CH_2-]_x$, obtained in the presence of organolithium compounds, have now been developed in the USSR by Korotkov et al.[204] These polymers are very similar to natural rubber not only in composition but also in their physical and mechanical properties, and thus represent a "synthetic natural rubber".

This rubber is known as SKI. In the USA it is termed Ameripol[205], Coral[206], or Natsin[207].

Polyisoprene prepared in the presence of alkyllithium catalysts contains 90% or more units linked in the 1,4-position and having a *cis*-configuration[15,23,45,204,206-208]. Similar products have been obtained in the presence of a Ziegler catalyst[205,207,209,210]. In this case, too, a polyisoprene is obtained which yields vulcanised rubbers with properties closely similar to those of products from natural rubber[209]. An interesting characteristic of this polyisoprene is the narrow molecular-weight distribution[211], which does not depend on the extent of conversion. This form of rubber is being greatly developed, and by 1965 some 25% of rubbers produced in the USSR will be polymers of isoprene[212]. They are used for the manufacture of car tyres and other articles previously made from natural rubber, which they are fully capable of replacing[209]. A road test of experimental car tyres containing SKI showed its high quality, little inferior to that of natural rubber[213].

A new rubber-like polymer, polydeuteroisoprene[214], has been obtained starting from deuteroacetone and deuteroacetylene:

$$(-CD_2-C(CD_3)=CD-CD_2-)_x.$$

The butadiene polymer prepared with Ziegler catalysts is of great interest. Natta[13] has shown that poly-*cis*-1,4-butadiene of extremely uniform structure is obtained. This polymer is characterised by highly elastic properties, surpassing in some respects even natural rubber[215]. It is known as "*cis*-1,4 rubber". Tests with tyres made of this rubber have shown that the wear resistance of the tread is 30–40% higher than when natural rubber is used. With tyres used by lorries there is a smaller production of heat[215].

Butadiene polymers can have different structures, depending on whether the units are combined in the 1,2- or 1,4-positions, and also on the presence of geometrical isomerism. Fig. 25 shows plane diagrams of four isomeric polymers of butadiene.

Among these, poly-*cis*-1,4-butadiene, whose chain conformation is depicted in Fig. 26, is of the greatest interest as a rubber. The other butadiene polymers, whose conformations are shown in Figs. 27–29, are of no interest as rubbers, but may be of interest from other points of view.

The carboxylate rubbers, an extremely interesting type of synthetic rubber, are copolymers of divinyl and other monomeric diolefins, and are obtainable in emulsion with monomers based on acrylic or methacrylic acid[216,217]. They can be obtained also by addition to a finished synthetic or natural rubber in solution or in a latex, or during processing on rollers such substances as thioglycollic acid, maleic anhydride, or acrylic acid[217]. Dolgoplosk and Tinyakova[218] prepared a carboxylate rubber by copolymerising methacrylic acid with butadiene or isoprene. Owing to the presence of free carboxy groups, carboxylate rubbers can be vulcanised not only with sulphur but also with metal oxides and diamines. Carboxylate rubbers surpass ordinary rubbers in mechanical properties, having a higher modulus and tensile strength and being more stable to ozone. They are employed for the manufacture of strong adhesives, and also for impregnating cord, fabrics, and paper.

Copolymers of butadiene and 2-methyl-5-vinylpyridine, or methylvinylpyridine rubbers, are characterised by high wear resistance. They have the name Philprene in the USA[219]. These rubbers have higher tensile strength and resistance to tearing and the widening of cuts than ordinary butadiene–styrene rubber[220]. The wear resistance of vulcanised methylvinylpyridine rubber is nearly twice that for divinylstyrene rubber: i.e. it approaches that for polyurethane rubber[221].

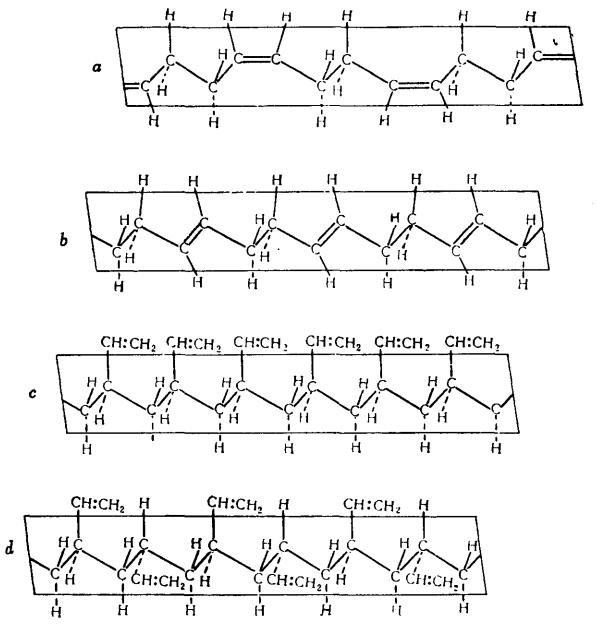


Fig. 25. Structure of isomeric polymers of butadiene: *a*) poly(*cis*-1,4-butadiene); *b*) poly(*trans*-1,4-butadiene; *c*) isotactic poly(1,2-butadiene); *d*) syndiotactic poly(1,2-butadiene).

Meyer, Gibbs, et al.[222] report a new class of elastomers with varied properties, obtained by treating latices of butadiene, chloroprene, butadiene–styrene, and other rubbers with alkanethiols in the presence of an initiator

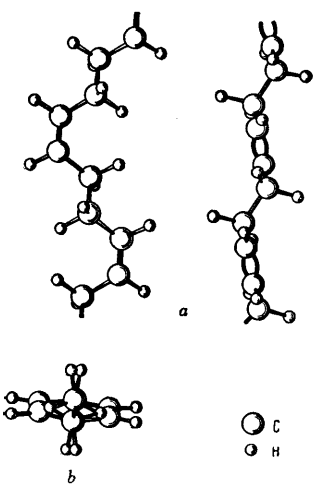


Fig. 26. Conformation of the chain of poly(*cis*-1,4-butadiene): *a*) side view; *b*) view from above.

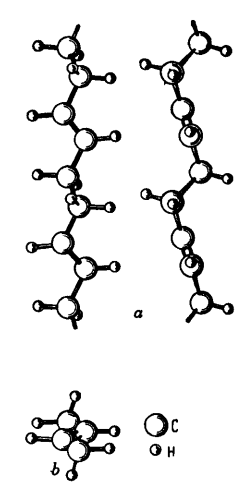


Fig. 27. Conformation of the chain of poly(*trans*-1,4-butadiene): *a*) side view; *b*) view from above.

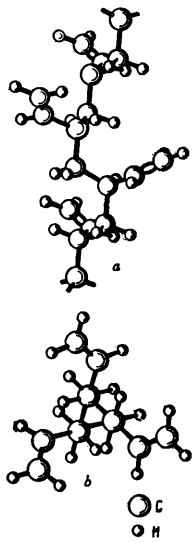


Fig. 28. Conformation of the chain of isotactic poly-(1,2-butadiene): *a*) side view; *b*) view from above.

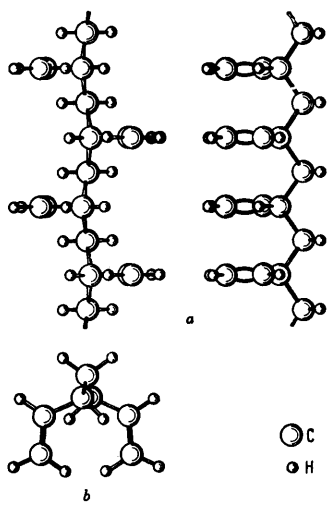


Fig. 29. Conformation of the chain of syndiotactic poly(1,2-butadiene): *a*) side view; *b*) view from above.

(usually azodiisobutyronitrile). In this process molecules of the thiol add on to the double bonds:

$$\cdots -CH_2-CH=CH-CH_2- \cdots \xrightarrow{CH_3SH} \cdots -CH_2-\underset{\displaystyle S\\ \displaystyle CH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{CH}}}-CH_2-CH_2- \cdots$$

The resulting products are characterised by increased saturation, are more stable to the action of ozone, and have increased resistance to heat, frost, solvents, and ageing.

Polyfluoroprene $[-CH_2-CF=CH-CH_2-]_x$ is a new polymer[223], which, in contrast to polychloroprene, possesses no rubber-like properties.

The liquid copolymer of butadiene and styrene linked in the 1,2-position has been suggested as a basis, instead of polyesters, for the production of glass-like plastics which are stable to hydrolysis[224].

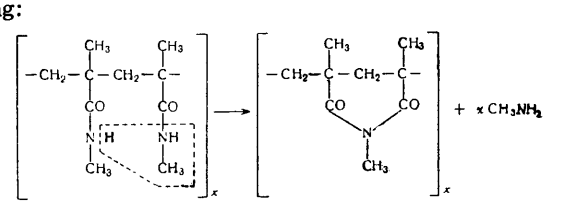
6. Polymers containing rings in the chain. The classical example of these polymers is phenol–formaldehyde resin. It has been suggested that, to eliminate its inherent defect of brittleness, it can be modified by mixing with such polymers as rubber[91-93] and polyamide[225], epoxy[226], and other resins. Various materials for corrosion protection, based on phenol–formaldehyde resins, have been made[227].

Recently Burke and Ruetman[228] described the production of linear phenol–formaldehyde polymers by the polycondensation of *o*-chlorophenol with formaldehyde in the presence of *p*-toluenesulphonic acid in a solution of bis-β-ethoxyethyl ether in an autoclave at 150°. These polymers can form fibres.

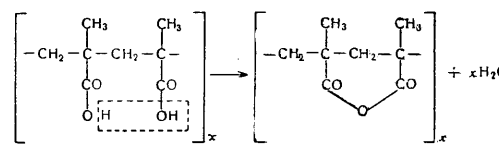
Great thermal stability and resistance to oxidation are characteristic of polymers containing benzene nuclei in the chain, such as polyphenylene $[-C_6H_4-]_x$[229], polyphenylene-ethyl or polyxylylene $[-CH_2-C_6H_4-CH_2-]_x$[118,119], polycarboxyphenylene $[-C_6H_3(COOH)-]_x$[229], polydiisopropylbenzene $[-C(CH_3)_2-C_6H_4-C(CH_3)_2-]_x$[120,121], polyperfluorophenylene $[-C_6F_4-]_x$[192], etc.

The introduction of rings into a chain generally results in an increase in the thermal stability of the polymers, as Bresler, Koton, et al.[117] have shown in the case of polymethylmethacrylamide and polymethacrylic acid.

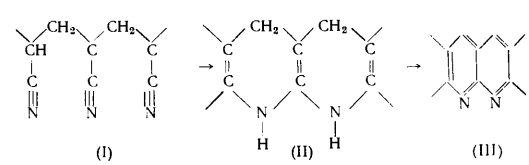
The former yields rings of the following structure on heating:



while the latter forms anhydride rings:



An interesting product is formed from polyacrylonitrile by heat treatment, the fibre being heated in air at 200°. The fibre blackens, becoming insoluble, and is not affected by the burner flame. Houtz[230] has shown that a polymer is obtained consisting of fused pyridine rings (III):



Topchiev et al.[231] studied the products formed by heating polyacrylonitrile and showed that they possess semiconducting properties. Fibres of this polymer are stable

at 400°. They are used for filtering concentrated sulphuric and hydrochloric acids, solutions of caustic soda, etc.

Recently great interest has been aroused by resins obtained from furfural and acetone. They are characterised by high thermal and chemical stability and have various uses, especially for "cementless" concrete[232].

Recently, flexible fibres and fabrics containing 99.9% graphite have been obtained[233]. They are prepared by carbonisation in a quite complex manner of such carbon-containing materials as cotton, viscose, rayon, etc., which are then converted into graphite by heating to 2980°. It is thus possible to convert any textile material into graphite form. These materials are suitable for reinforcing plastics to be used at high temperatures, for the manufacture of filter hose for hot non-oxidising gases, equipment for transporting corrosive liquids, high-temperature thermal insulation, etc.

B. Heterochain Polymers

1. Polyethers. Previously only one representative of this group, poly(ethylene oxide), was widely known, but now we are acquainted with several polymers of this type.

Polyformaldehyde $[-CH_2-O-]_x$, although it has been known for a long time, could not be obtained with a sufficiently high molecular weight, in spite of the fact that Staudinger[234] as early as 1929 reported the preparation of fibre-forming polymers of formaldehyde. Recently, formaldehyde polymers of high molecular weight, with extremely interesting properties, have been prepared[235-238]. Polyformaldehyde has m.p. 185°, sp. gr. 1.25, and high mechanical strength[236]. It readily crystallises. A peculiarity of polyformaldehyde is its high impact strength, which is of great practical interest. Because of the availability of the starting materials and the excellent mechanical properties, polyformaldehyde will undoubtedly have an immense field of application in the near future[236]. At present it is used in the manufacture of a synthetic fibre known as Delrin, which has a strength of 4 g/denier at an elongation of 11%. The comparatively low strength of the synthetic fibres is explained by the fact that only a fraction of the macromolecules in the fibre effectively resist rupture, as can be seen from Fig. 30.

A peculiarity of the polymerisation of formaldehyde is the necessity for using very pure monomer, since the presence of even minute amounts of impurity prevents the production of polymers of sufficiently high molecular weight[235], the presence of moisture being especially harmful. Concentrated sulphuric acid is used for the dehydration and purification of the monomer. The polymerisation catalysts are boron fluoride, triethylamine, sulphur trioxide, and also the carbonyls of iron, nickel, and cobalt, and such organometallic compounds as diphenyltin, triphenylbismuth, and phenylmagnesium bromide, calcium hydride, etc. The formaldehyde enters the solvent (benzene), to which the catalyst has been added, at the same rate at which polymerisation occurs. The polymer formed separates as a precipitate and is filtered off[235]. Polyformaldehyde is characterised by great strength. Table 9 gives the fundamental physical properties of Delrin.

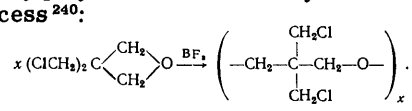
Polyacetaldehyde, suitable for the manufacture of articles, has recently been synthesised in Japan. It is obtained by polymerising acetaldehyde in the presence of an aluminium oxide catalyst[239]. Polyacetaldehyde is an

TABLE 9. Physical properties of Delrin[236].

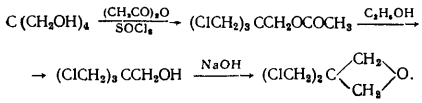
Property	Value
Elongation, %	
at 23°	16
at 70°	330
Specific impact strength, kg/cm	
at 4.5°	6.55
at 23°	7.63
Tensile strength, kg/cm²	
at 23°	700
at 70°	525
Modulus of elasticity under static bending, kg/cm²	
at 23°	28 700
Static-bending strength, kg/cm²	
at 23°	990
Fatigue limit at 23° and 100% relative humidity, kg/cm²	350
Shear strength, kg/cm²	666
Heat resistance, °C	
at 18.5 kg/cm²	100
at 4.62 kg/cm²	170
Deformation under load, % (140 kg/cm² at 50°)	0.5
Compressive stress at 1% deformation, kg/cm²	364
Moisture absorption, %	
on immersion in water for 24 h	0.4
at 50% relative humidity	0.2
Specific gravity	1.425
Rockwell hardness, M94	120
Flammability, cm/min	2.8
Softening point of crystalline polymer, °C	175
Yield point, °C	184
Coefficient of linear expansion	0.000081
Thermal conductivity, kcal/m²deg h cm	3 08
Specific heat, cal/g	0.35

elastomer, surpassing butadiene–styrene rubber in heat resistance. It is vulcanised under the influence of radiation.

An interesting new polymer is that of 3,3-bischloromethyloxacyclobutane, bearing the trade name Penton. It is obtained by polymerisation of the cyclic ether by the following process[240]:



The original monomer is synthesised from pentaerythritol via a series of intermediate stages:



The polymerisation is carried out in a solvent (methyl chloride, chloroform) in the presence of boron trifluoride at 0° and below[241]. Penton melts at 180°. Its glass temperature is 7.5°. It can be made into films, fibres, and

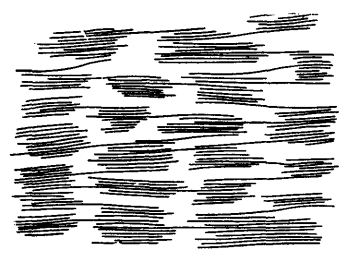
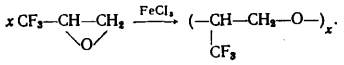


Fig. 30. Arrangement of macromolecules in a fibre.

plastics by extrusion[242,243]. Penton is a similar material to poly(vinyl chloride), but is more stable to heat and the action of chemical reagents.

Among other polymeric ethers must be mentioned the polymer of 1,1,1-trifluoro-2,3-epoxypropane, obtained in the presence of ferric chloride:



It is characterised by high thermal stability, is insoluble in hydrocarbons and halogenated derivatives[244], and is soluble in acetone.

Epoxy resins form a large group of substances obtained by reaction of various diphenols with epichlorohydrin and analogous alkylene oxides[245]. Thus dicyclopentadiene dioxide yields resins which are stable up to 300°. The ease of preparation of these polymers, their strong adhesion to various materials, and the great strength of articles made from them have led to the wide employment of epoxy resins in various fields[246].

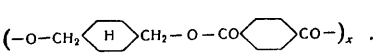
Great interest attaches to epoxy resins modified with polyamides[247,248]. They are used as film-forming materials or adhesives. Mixtures of epoxy resins with phenol–formaldehyde resins are also of interest[226]. Recently copolymers have appeared of epoxy resins with organosilicon resins, which retain their mechanical and electrical strength up to 200°–250°.[249,250]

2. Polyesters. These have long been widely employed in the paint and varnish industry, where in the form of alkyd resins they constitute ~ 50% of all film-forming materials used[251]. A huge number of different polyesters are now known[252].

Comparatively recently poly(ethylene terephthalate) $[-CH_2CH_2OCOC_6H_4COO-]_x$ has been obtained, and under such names as Lavsan, Terylene, Dacron, Mylar, Melinex, etc. has been widely employed for the production of synthetic fibres and films which are distinguished by outstanding strength and heat resistance. Films of Lavsan have exceptional strength, and are used as a basis for cinematograph films, for electrical insulating purposes, and also in various branches of technology[253].

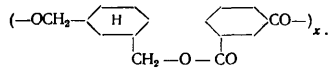
Several copolymers have been suggested for fibre production — mixed polyesters containing together with terephthalic acid and ethylene glycol also sebacic acid (10%)[254] or isophthalic acid (10–15%)[255]. The latter copolymer is termed Videne.

Recently production has begun of a new type of fibre (Kodel) based on a polyester of terephthalic acid with hydrogenated *p*-xylylene glycol:



The polyester melts at 270° and withstands heating up to 218°; it is used mixed with other fibres[256], and articles made from it do not crease and do not acquire an electrostatic charge.

The polyester of isophthalic acid and hydrogenated *m*-xylylene glycol (m.p. 200°) has been proposed for the manufacture of films:



Rubber-like properties are possessed by polyesters of fluorinated glycols and dicarboxylic acids[186]. Poly(hexafluoropentamethylene adipate) $[-OCH_2[CF_2]_3CH_2OCO[CH_2]_4.CO-]_x$ has a working temperature range from -72° to +150°. It is closest in properties to natural rubber compared with other fluorinated elastomers. It is resistant to benzene[177], and can be vulcanised with peroxides in the presence of carbon black.

An interesting form of rubber is represented by the polyester–urethanes, obtained by the reaction of 2,4-tolylene diisocyanate with a branched polyester of an aliphatic dicarboxylic acid (adipic, etc.) and an aliphatic glycol or mixture of glycols (butylene glycol, ethylene glycol, trishydroxymethylpropane, etc.) or even with a polyether of sufficiently high molecular weight[257].

Polyester–urethanes are produced on an industrial scale under the names Adiprene (USA), Vulkollan (Western Germany), Chemigum (USA). A distinctive feature of rubbers of the Adiprene type is their exceptionally high abrasion resistance, in which they surpass all other rubbers; therefore the main application of polyester–urethanes is the manufacture of tyre treads and other parts which are subject to friction[258,259]. Losev and Datskevich[260] prepared a series of polyester–urethanes, and determined how their properties varied with the nature of the starting materials.

Great interest attaches to polyesters of carbonic acid and various diphenols, the polycarbonates, which represent a new type of polymer, distinguished by great strength, heat stability, and especially outstanding impact strength[261]. The most widely used among these products is the polymer prepared from carbonyl chloride and 2,2-bis(4-hydroxyphenyl) propane:



Phosphoric esters are added during the reaction to obtain a colourless product. This polymer is known under the trade name Lexan[262]. It melts at 268°, softens at 140°, and is characterised by high impact strength, forty times as great as that of polystyrene. It is used for the manufacture of film, especially photographic film, bulky goods, electrical insulation, etc.

The "polyarylates" are very interesting, comprising polyesters of various dicarboxylic acids and dihydric phenols[263–265]. They are distinguished by high thermal stability, which may reach up to 500°, and possess great mechanical strength. They are prepared by the reaction of chlorides of dicarboxylic acids with dihydric phenols:

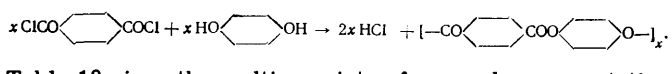


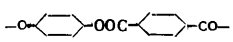
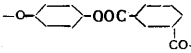
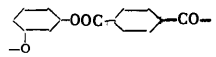
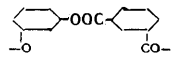
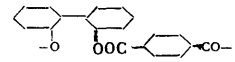
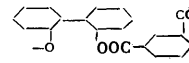
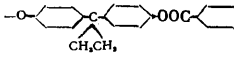
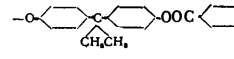
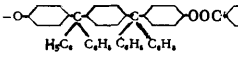
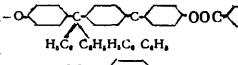
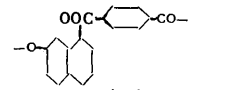
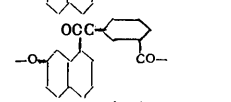
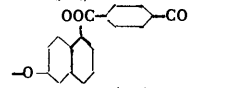
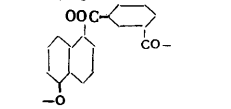
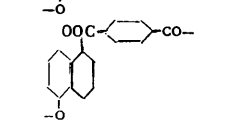
Table 10 gives the melting points of several representatives of the polyarylates.

Polyarylates dissolve appreciably only in tetrachloroethane, being insoluble in water and in other organic solvents. A series of mixed polyarylates have been prepared, whose properties can thus be varied over a wide range[264,265]. Polyarylates have also been obtained from various phosphinic acids[266], and are distinguished by their non-inflammability.

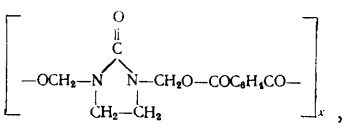
Conix[267] has described a large number of polyesters obtained from bisphenols, having the structure $HOC_6H_4RC_6H_4OH$, and dicarboxylic acids, and also polyesters of the general formula $[-COC_6H_4RC_6H_4COOC_6H_4RC_6H_4O-]_x$ with various radicals.

Some of the polyesters are of interest because of their

TABLE 10. Melting points of polyarylates [263].

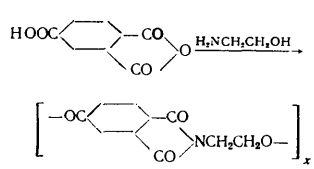
Acid	Dihydric phenol	Structural unit	M.p., °C
Terephthalic	Quinol		above 500
Isophthalic	Quinol		320
Terephthalic	Resorcinol		270
Isophthalic	Resorcinol		230
Terephthalic	o,o'-Dihydroxybiphenyl		172
Isophthalic	o,o'-Dihydroxybiphenyl		158
Terephthalic	p,p'-Dihydroxydiphenylpropane		350
Isophthalic	p,p'-Dihydroxydiphenylpropane		275
Terephthalic	1,4-bis(4'-hydroxyphenyldiphenylmethyl)benzene		220
Isophthalic	1,4-bis(4'-hydroxyphenyldiphenylmethyl)benzene		157
Terephthalic	1,7-Dihydroxynaphthalene		230
Isophthalic	1,7-Dihydroxynaphthalene		188
Terephthalic	1,6-Dihydroxynaphthalene		above 500
Isophthalic	1,5-Dihydroxynaphthalene		above 500
Terephthalic	1,5-Dihydroxynaphthalene		above 500

high melting points, among them being the polyester of terephthalic acid:

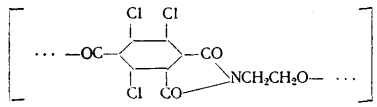


melting at 340°.

The polyester of trimellitic acid and monoethanolamine [268] melts at 350°. It is prepared by the following reaction scheme:



Still more thermostable is the analogous polyester of chlorinated trimellitic acid:



A large number of di- and tri-allyl esters of various polycarboxylic acids have been prepared. These polyesters are used together with those of unsaturated acids in the production of glass textolites [53,269].

A copolymer of the polyester of 1,3-butylene glycol and maleic acid with styrene is of considerable interest as electrical insulating material distinguished by high resistance to arcing [270].

Great interest attaches to alkyd resins based on isophthalic acid. They yield a stronger and more lustrous film than alkyds based on phthalic acid [271].

3. Polysulphones. Noether [272] prepared a series of polysulphones by means of the reaction

$$x\,\mathrm{NaS(CH_2)_m SNa} + x\,\mathrm{Br(CH_2)_n Br} \rightarrow 2x\,\mathrm{NaBr} + [-\mathrm{S(CH_2)_m S(CH_2)_n}-]_x \quad ,$$

$$[-\mathrm{S(CH_2)_k}-]_x + \mathrm{H_2O_2} \rightarrow [-\mathrm{SO_2(CH_2)_k}-]_x .$$

Poly(hexamethylene sulphone) melts at 220°. Fibres which are not inferior to polyamides in strength are made from polysulphones. They are readily dyed with Cellon dyes.

4. Polyanhydrides. Conix [273] prepared polyanhydrides of aromatic dicarboxylic acids of the type $HOOCC_6H_4O[CH_2]_xOC_6H_4COOH$. Polyanhydrides have proved to be good film- and fibre-forming substances, stable in the molten state to the action of oxygen and resistant to moisture and aqueous alkalis. A fibre can be made from them.

5. Polyamides. There is a general relation, established by Korshak and Frunze [274], between the melting points of heterochain polyamides and their chain structure. Korshak and Frunze found that the melting point is related to the number of methylene groups in a chain unit by the equation $y = ax + b$, where y is the melting point of the polyamide, x is a heterochain characteristic representing the ratio of the number of groups containing hetero atoms to the number of methylene groups expressed as a percentage, and a and b are constants characteristic of each series of polyamides (b = 110). Fig.31 shows plots for series of polyamides, polyesters, and polyanhydrides, showing the relation between the melting point and the heterochain characteristic [275]. Table 11 gives values of the constants and the equations for various groups of polymers.

Previously known representatives of heterochain polyamides are polyhexamethyleneadipamide, known as Anid or 6,6-nylon, and poly-ε-caprolactam, termed Capron, Perlon, or 6-nylon. Many new representatives of this group have now appeared, applicable as starting materials for synthetic fibres, and also as film-forming materials, and for the production of plastics [276]. It is interesting that laminated plastics based on phenolic resins reinforced with polyamide fibre have considerably better heat resistance than analogous glass-like plastics [277].

Strepikheev, Nesmeyanov, Freidlina, and other investigators developed Enant, a new form of synthetic fibre made

TABLE 11. Equations for various types of polymers[275].

Polymer group	Equation
Polyureas with an even number of methylene groups in the unit	$y=8.4x+110$
Polyamides with an even number of methylene groups in the unit	$=7x+110$
As above (from other data)	$y=7x+125$
Polyamides from dicarboxylic acids with an odd number and diamines with an even number of methylene groups	$y=6.2x+110$
Polyamides from dicarboxylic acids with an even number and diamines with an odd number of methylene groups	$y=5.6x+110$
Polyamides from dicarboxylic acids and diamines with odd numbers of methylene groups	$y=4.5x+110$
Polyurethanes with an even number of methylene groups in the unit	$y=3.5x+110$
Polyamides containing sulphide sulphur in the chain	$y=3x+110$
Polyamides containing ether oxygen in the chain	$y=1.9x+110$
Polyanhydrides with an even number of methylene groups in the unit	$y=2.5x+110$
Polyesters with an even number of methylene groups in the unit	$y=3x+110$
Polyesters with an odd number of methylene groups in the unit	$y=3.6x+110$
Polyanhydrides with an odd number of methylene groups in the unit	$y=3.6x+110$

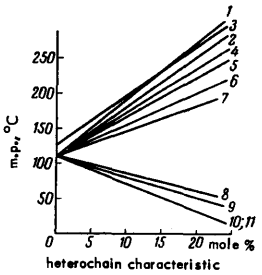


Fig. 31. Variation in melting points in the series: 1) polyureas; 2) polyamides with an even number of methylene groups in the diamine and in the acid; 3) as above, according to more accurate data; 4) polyamides formed from a diamine with an even number and an acid with an odd number of methylene groups; 5) polyamides from diamines with an odd number and acids with an even number of methylene groups; 6) polyamides from diamines and acids with odd numbers of methylene groups; 7) polyurethanes; 8) polyanhydrides with an even number of methylene groups in the structural unit; 9) polyesters from glycols and acids with even numbers of methylene groups; 10) as above, with an odd number of methylene groups in the acid; 11) polyanhydrides with an odd number of methylene groups in the structural unit.

from poly-ω-heptanamide $[-NH[CH_2]_6CO-]_x$. Enant fibre is characterised by high tensile strength and is especially resistant to double flexing[278].

Nesmeyanov and Freidlina[279] prepared ω-aminoheptanoic acid, starting from ethylene, by telomerisation with carbon tetrachloride:

$$R\cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3,$$

$$\cdot CCl_3 + CH_2{=}CH_2 \longrightarrow Cl_3C-CH_2-CH_2\cdot \xrightarrow{+2CH_2=CH_2} Cl_3C(CH_2CH_2)_3\cdot,$$

$$Cl_3C(CH_2CH_2)_3 + CCl_4 \longrightarrow Cl_3C(CH_2)Cl + \cdot CCl_3,$$

$$Cl(CH_2)_6CCl_3 \xrightarrow[H_2SO_4]{H_2O} Cl(CH_2)_6COOH \xrightarrow{NH_3} H_2N(CH_2)_6COOH.$$

The formation of ω-aminoheptanoic acid in this reaction is accompanied by that of ω-aminononanoic and ω-aminoundecanoic acids, which are used to prepare two new types of synthetic fibres, Pelargon $[-NH[CH_2]_8CO-]_x$ and Undekan $[-NH[CH_2]_{10}CO-]_x$ (Rilsan)[278].

Among the large number of polyamides containing sulphur in the chain, that from thiodivaleric acid and hexamethylenediamine (m.p. 180°) has proved suitable for fibre production[280]. The fibre from this polyamide possesses increased elasticity and is of great interest for the production of staple fibre[281] since thiodivaleric acid, obtained from ethylene and carbon tetrachloride, is readily available[282].

A fibre from polypyrrolidone[283] known as 4-nylon absorbs water more strongly and is more easily dyed than 6- or 6,6-nylon.

A series of polyamides containing siloxane groups in the chain have been synthesised from acids of the structure:

$$HOOC-(CH_2)_2Si(R)_2-O-Si(R)_2-(CH_2)_2-COOH,$$

where R = CH_3, C_2H_5. These polyamides are characterised by rubber-like properties[284].

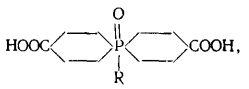
A series of polyamides, distinguished by their high melting points, have been synthesised from *p*-xylylenediamine and dicarboxylic acids[285]. If *trans*-isomers of hydrogenated diamines are employed, very high-melting polyamides can be obtained[286], whereas *cis*-isomers yield amorphous polyamides melting at lower temperatures.

A series of high-melting polyamides have been obtained from terephthalic and isophthalic acids with aliphatic and hydroaromatic diamines[287].

A large number of copolymers have been prepared and used as starting materials for the production of a synthetic fibre (Trelon)[288] and as film-forming materials (Anid G-669[289], etc.). A good solvent for polyamides has recently been found in trifluoroethyl alcohol[290].

Fedotova et al.[291] have prepared a number of polyureas $[-CONHRNHCOR'-]_x$ by the interaction of diamines with diisocyanates; these are strong materials with excellent dielectric properties.

Interesting organophosphorus polyamides are obtained by the polycondensation of diamines with carboxylated phosphine oxides, e.g.:



where R = CH_3 or C_6H_5. These polymers are capable of fibre formation and are completely non-inflammable[292-294].

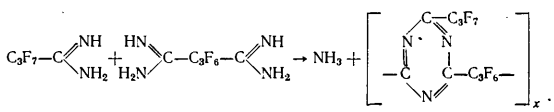
Combinations of polyamides with epoxy[247,248], phenol–formaldehyde[225], and urea– or melamine–formaldehyde resins, chlorosulphonated polyethylene, etc. have been widely used as coating materials, adhesives, etc.[247,295]

The application of polyamides to the production of laminated asbestos sheets, which withstand a temperature of above 1000° for 5 min, has been described[296].

Synthetic polypeptides are being increasingly studied; they are obtained by the decomposition of anhydrides of α-amino-acids and other compounds. These researches approach more and more closely to the synthesis of proteins, on which are based the vital processes of living beings. However, the preparation of proteins similar to those occurring in organisms is undoubtedly a very complicated problem, since the twenty amino-acids encountered in natural proteins with a molecular weight of 100 000 (which corresponds roughly to a degree of polymerisation of 1000) can yield 10^{1200} differently constructed molecules. To give

an idea of what this figure means, we may mention that the total number of atoms in the Earth is only 10^{50}.

A very interesting polymer, characterised by elasticity and great thermal stability, was obtained by Braun[186] by the pyrolysis of a perfluoromonoamidine with a perfluorodiamidine:



This polymer chain obviously contains triazine rings linked by perfluorotrimethylene groups. The polymer withstands heating up to 540°.

A polymeric triazine, obtained by the condensation of pentafluorobenzamidine with perfluorophthaloyldiamidine, has been described[192].

6. Organometallic and analogous polymers ("organo-elemental" polymers). These substances have been attracting increasing attention from investigators looking for materials of high thermal stability and with other qualities. Nesmeyanov[145,297] has made a detailed examination of various elements of the Periodic System from the point of view of the possibility of combining them with organic radicals to form polymers.

During the past few years various polymeric systems containing inorganic molecular chains have been studied[298]. Special attention has been paid to polymers containing the following structural units[186]:

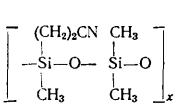
—B—N—B—N—	—Si—O—Al—
—B—P—B—P—	—P—N—P—N—
—Al—P—Al—P—	—C—N—C—N—
—P—O—P—O—	—S—N—P—
—Si—O—B—	—Sn—O—Sn—
—Si—O—Sn—	—Sn—S—Sn—
—Si—O—P—	R_f—X—R_f(X=O, N, P, S, metal)

coordination (chelate) polymers

The purpose of these investigations was to obtain polymers of great thermal stability (to 500° and above).

7. Polysiloxanes. Among organometallic and analogous polymers the most important are the organosilicon compounds, research on the synthesis and application of which has been intensively developed[299]. These compounds have been widely used in the form of silicone oils, rubbers, and varnishes[300].

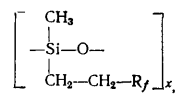
Recently new types of organosilicon polymers have appeared, in which great strength has been achieved by the introduction of nitrile groups. These are the nitrilosilicone rubbers[301,302], containing the nitrile groups in the alkyl radical attached to silicon, and may be represented by the general formula



They constitute copolymers of dimethylsilicone and methylcyanoethylsilicone rubbers. Other combinations are also possible. These rubbers are extremely resistant to oils and boiling hydrocarbons, their swelling is only 10% of that of ordinary methyl silicone rubber, and they are very strong over the temperature range from -70° to +260°.

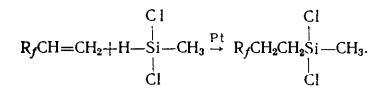
A very interesting group of organosilicon polymers is formed by the fluorosilicones, containing fluorinated alkyl groups attached to the silicon atoms. Their heat resistance is considerably greater than that of the alkylsilicon compounds.

Fluorosilicone rubbers have the structure[186]:



where $R_f = CF_3$, C_2F_5, C_3F_7.

The original monomers are obtained by addition of methyldichlorosilane to an olefin:

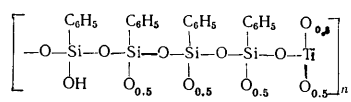


On the basis of these monomers, fluorosilicone rubber, poly(methyl-3,3,3-trifluoropropylsiloxane) (Silastic, LS-53), possessing good characteristics[177,303], has been evolved. Its brittle point is -68°, its operating temperature is 200°, and it has great resistance to oils. However, vulcanised fluorosilicone rubbers have low strength, and are therefore employed for making packing washers, sleeves, diaphragms, airtight seals, etc.

Polymers obtained from silanols, containing such unsaturated groups as vinyl[304], are of considerable interest. They are readily vulcanised and yield stronger rubbers.

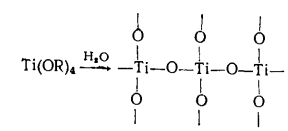
Andrianov has prepared polymers containing a chain of silicon, oxygen, and metal atoms[305], e.g. —Si—O—Al—O—, which are termed "aluminosiloxanes"; they are characterised by great thermal stability[306].

A still stronger bond is —Si—O—Ti—, which occurs in polytitano-organosiloxanes:



They have still greater heat resistance and hydrolytic stability than the polyaluminosiloxanes[307].

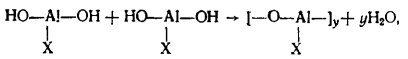
8. Polytitanoxanes. Among high polymers of other elements, practical use has been found for polymers of titanium oxide, prepared by hydrolysis of orthotitanic esters:



They form very strong films and are employed in the optical industry[308].

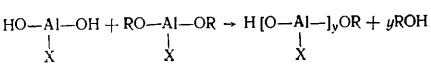
Mixed products have been obtained, containing silicon and titanium, by combination of a silicone polymer with esters of orthotitanic acid[307,308]. A Ti—O—Si bond is obviously formed in these compounds; they can be cold-hardened and yield strong films, which are suitable as coatings for ceramic electrical insulators and for imparting water-repellent properties to the walls of buildings[309].

9. Polyaluminoxanes. The preparation has been described of polymeric basic aluminium salts of organic acids[301], obtained by elimination of water from the basic salt

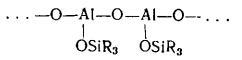


where X is a radical of stearic or other organic acid.

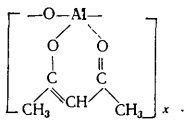
The starting materials can be the basic salt and a dialkoxyaluminium salt[311]:



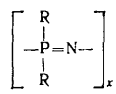
A new variety of compounds of this type is represented by the polyorganosiloxanoaluminoxanes prepared by Andrianov and Zhdanov[312]:



Interesting complex polymers have been obtained by Kugler[313] by the hydrolysis of a dialkoxyaluminium acetylacetonate, the macromolecule of which is made up of the following units:

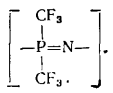


10. Organophosphorus polymers. Among phosphorus-containing polymers great attention has been paid to the group of substances based on a chain of phosphorus and nitrogen atoms[314]:



The first member of this group, which has been known for a long time, poly(phosphoronitrile chloride) $[-PCl_2=N-]_x$, possesses great thermal stability (~300°) and is a rubber-like material.

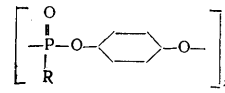
An interesting product is poly(phosphoronitrile fluoride), which is distinguished by great thermal stability[315]. A series of compounds have been obtained in which the phosphorus bears alkyl, aryl, alkoxy, aroxy, alkylamino, and arylamino groups. Many of them have high melting points[316]. An interesting derivative is the trifluoromethyl polymer which is an elastomer:



The use of phosphoronitrile polymers as additives to increase the thermal stability of phenolic and other resins has been suggested. Introduction of such additives enables these resins to be employed for the manufacture of brake shoes, various frictional materials, abrasives, etc.[314]

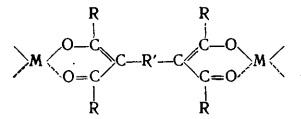
Linear phosphinoborines, containing a chain of phosphorus and boron atoms $[-P-B-]_x$, form a very heat-resistant plastic, with a molecular weight of 12 500, which withstands a temperature of up to 400°.[317]

In addition, a large number of organophosphorus polymers belonging to the polyester and polyamide groups have been prepared. Thus, a series of polyesters have been obtained from alkyl- and arylphosphinic acids with various glycols and diphenols[318]:



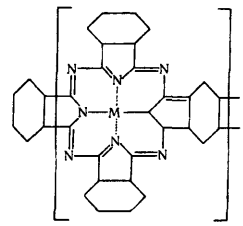
These compounds do not burn and can be used as coatings.

11. Coordination polymers. Examples of these interesting polymers are the complexes of tetraketones with copper, cadmium, zinc, and other metals, which have chains of the following structure[139,142]:

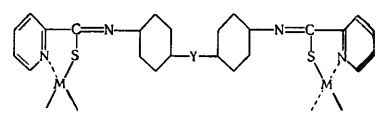


These compounds have different colours and high melting points (300° and above).

The phthalocyanine complexes of copper and other metals, described by Marvel and his collaborators[287,319] are still more heat-resistant. From pyromellitic acid, phthalic anhydride, and urea or from 3,3',4,4'-tetracyanodiphenyl ether and the latter two compounds they prepared a series of polymers of the type



Martin[279,322] prepared a series of complex polymers from bis(thio-α-picolinamide) compounds of the type



12. Inorganic polymers. Many substances belonging to this last group of polymers[320] are widely used in industry, but they are all natural products. Recently a number of synthetic inorganic polymers have been obtained and have already found several fields of application. Among them must be mentioned synthetic diamond, sapphire, alexandrite, ruby, mica, asbestos, and similar materials.

Borazon[321] can be cited as an interesting example. Ordinary boron nitride is softer than diamond and has a hexagonal structure. If it is subjected to a pressure of 70 000 kg/cm², its crystal structure becomes cubic. The Borazon thus obtained is harder than diamond and will scratch the latter. It withstands a temperature up to 1800°, whereas diamond burns at 870°.

An interesting product is Pyroceram, a vitreous material characterised by great heat-resistance and mechanical strength[323].

IV. CONCLUSION

In conclusion it must be remarked that even a cursory review of new polymers such as this shows that the large number of new high polymers now existing provide extensive opportunities for a fuller satisfaction of the needs of modern technology. The problem consists in utilising these new materials for the production of various goods.

Our survey of the achievements of synthetic polymer science also shows that the further development of synthetic methods undoubtedly promises to yield still more new polymeric compounds with new properties; their development is a most important task of macromolecular chemistry.

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ANIONIC POLYMERISATION IN THE PRESENCE OF ALKALI METALS AND THEIR COMPOUNDS

A. R. Gantmakher and Yu. L. Spirin

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INTRODUCTION

Anionic polymerisation processes are of considerable interest, since they enable us to synthesise polymers with valuable properties, e.g. polymers of regular structure, such as *cis*- and *trans*-polyisoprene, isotactic polystyrene, isotactic and syndiotactic methyl methacrylate, etc., and also block copolymers.

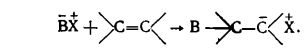
The catalysts for anionic polymerisation are substances of basic, electron-donor character — alkali metals and their amides, various organometallic compounds, complex organometallic compounds, organomagnesium compounds, etc. Anionic polymerisation of very reactive monomers is also brought about by water, alkalis, amines, and alkali-metal carbonates and bicarbonates.

The present review is concerned mainly with polymerisation in the presence of alkali metals and their derivatives.

The monomers most active in anionic polymerisation are compounds containing electronegative substituents attached to a double-bonded carbon atom — vinylidene cyanide, nitroethylene, acrylonitrile, methyl acrylate, methacrylonitrile, methyl methacrylate, etc. The polymerisation takes place by an ionic mechanism of the acid—base type[1], the catalysts or active centres acting as electron donors, and the monomers as electron acceptors.

Under the influence of an anionic catalyst BX an active

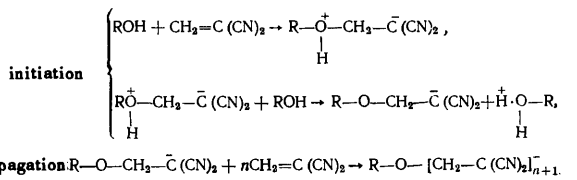
growth centre is formed by the reaction



This active centre is a tervalent negatively charged ion of carbon, a carbanion; in weakly polar media a positive gegenion is always present in the field of the carbanion, forming with it an ion pair.

I. POLYMERISATION BROUGHT ABOUT BY WATER, ALCOHOLS, AND AMINES

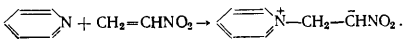
Monomers which are very active in anionic polymerisation — vinylidene cyanide and nitroethylene — polymerise in the cold in the presence of water, alcohols, and amines[2,3,4]. The proposed mechanism of polymerisation is represented by the scheme



Gilbert et al.[5] observed that polymerisation of vinylidene cyanide occurs in the presence of isobutyl vinyl ether, which acts as the base, while the vinylidene cyanide acts as the acid. With these two monomers present together, anionic and cationic polymerisation occurred simultaneously. Polymers of two types separated out, one soluble in benzene and having a high content of isobutyl vinyl ether, formed by cationic polymerisation, and the other insoluble in benzene and with a high content of vinylidene cyanide, formed by an anionic mechanism. On addition of triethanolamine to the system, the cationic polymerisation was suppressed, and no formation of benzene-soluble polymer was observed. Introduction of phosphorus pentoxide into the system inhibited the anionic polymerisation of the vinylidene cyanide.

The polymerisation of nitroethylene in the presence of pyridine in ethyl methyl ketone was studied by Vofsi and Katchalsky[6,7], who found the rate of reaction to be proportional to the concentration of pyridine and to the square of the concentration of monomer. The molecular weight hardly varied with change in the monomer concentration, indicating the occurrence of chain transfer with the monomer, and was independent of the concentration of catalyst.

These workers suggest the following initiation mechanism:



This process has a negative activation energy, -1.5 kcal/mole.

II. POLYMERISATION IN THE PRESENCE OF ALKALI METALS, THEIR AMIDES, AND ORGANIC DERIVATIVES

The polymerisation of unsaturated compounds by means of metallic sodium was observed by Karakau[8] in the case of styrene as long ago as 1878. The possibility of polymerising diene hydrocarbons with alkali metals was first established by Kondakov[9].

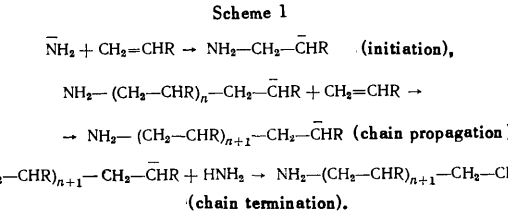
Subsequently Matthews[10] and Harries[11] suggested a method for polymerising diene hydrocarbons with metallic sodium, and Lebedev[12] originated a method for obtaining synthetic rubber from butadiene using metallic sodium as catalyst. Ostromyslenskii[13] showed that unsaturated compounds could be polymerised with organosodium derivatives. Subsequent research on the laws governing these reactions has made it possible to clarify the nature of such processes.

A. Polymerisation in the Presence of Alkali-Metal Amides in Liquid Ammonia

In a study of the polymerisation of various monomers with butylmagnesium bromide and triphenylmethylsodium Beaman[14] found that the resulting copolymer contained groups originally present in the initiator.

The investigations of Sanderson and Hauser[15] and of Higginson and Wooding[16] on the polymerisation of styrene with potassamide in liquid ammonia showed that each polymer molecule contains an NH_2 group. The rate of polymerisation of styrene was proportional to the square of the concentration of monomer and to the concentration of amide ion. The molecular weight of the polymers was independent of the catalyst concentration but was proportional to the concentration of styrene. Molecular weights determined viscosimetrically and cryoscopically were in good agreement with values calculated from analytical results for the nitrogen content on the assumption that every polymer molecule contains a single NH_2 group. On the basis of these results the following mechanism was proposed for the process occurring in the presence of alkali-metal amides in liquid ammonia:

Scheme 1



Thus chain termination occurs by elimination of a proton from an ammonia molecule with regeneration of the catalyst, the amide ion.

From the temperature variation of the rate of polymerisation of styrene and of the molecular weight of the resulting polystyrene, an estimate was made of the activation energies of the individual stages in this process:

$$E = E_i + E_p - E_t + {}^1/_2\,\Delta H \text{ (diss. } KNH_2) = 9 \pm 2 \text{ kcal},$$

where E is the overall activation energy, E_i the activation energy of initiation, E_p that for propagation, and E_t the activation energy of chain termination. It was found that ΔH (diss. KNH_2) = 0 ± 2 kcal/mole and $E_p - E_t$ = = -(4 ± 1) kcal/mole. By subtracting these quantities from the value of E, a value of 13 ± 4 kcal/mole was obtained for the activation energy of initiation E_i.

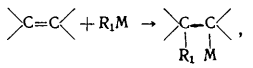
Polymerisation of acrylonitrile, methyl methacrylate, and methacrylonitrile also occurred with alkali-metal amides in liquid ammonia. Butadiene did not polymerise under these conditions, possibly because its solubility in liquid ammonia is low. α-Methylstyrene and diphenylethylene did not polymerise with alkali-metal amides in

liquid ammonia, but reacted with the amide ion with the formation of the corresponding carbanions, the solution becoming red.

These results show that anionic polymerisation in the presence of a proton-donor solvent is accompanied by a chain-terminating reaction. In such systems the molecular weight of the polymers is proportional to the concentration of monomer and is independent of the concentration of catalyst.

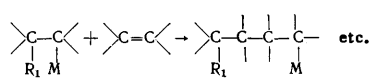
B. Polymerisation in the Presence of Alkali Metals and their Organic Derivatives*

An investigation of the reaction products formed by organometallic compounds with unsaturated molecules led Ziegler and Bahr[17] to the conclusion that the organometallic compound adds on to the double bond as follows:



where M represents an alkali metal.

The polymerisation can be regarded also as a process of successive entry of monomer into the organometallic compound at the R–M bonds by addition of R and M to the double bond of the unsaturated compound:

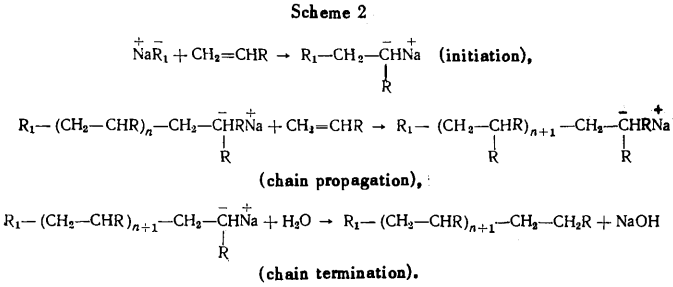


It was shown that an organometallic compound of high molecular weight is formed by such a process.

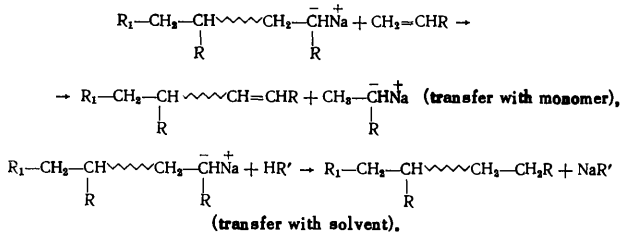
On analysing their own results and those of Schlenk[21], Ziegler and Bähr concluded that polymerisation in the presence of alkali metals occurs in a similar manner, the primary organometallic compound being formed by addition of sodium to the unsaturated molecule. Further investigations showed that the polymerisation of unsaturated compounds with alkali metals and with their organometallic compounds in polar solvents occurs by an anionic mechanism, the active centre under these conditions being the ion pair $\bar{R}\overset{+}{M}$ or a free carbanion.

The individual steps in such a process are shown in scheme 2 for an organosodium catalyst.

Scheme 2



Chain termination takes place in the presence of proton-donor compounds or molecules of the type RX (where X = Cl, Br, I, OH, etc.). Chain-transfer reactions are also possible:



It is evident from this scheme that the structure of the active-growth centre differs little from that of the original organometallic compound, only the organic radical linked to the metal being different. Depending on the nature of the radical in the original organometallic compound, the rate of initiation can be less than, equal to, or greater than the rate of growth of the chain. For example, in the polymerisation of styrene in the presence of triphenylmethylsodium, the rate of initiation is less than that of chain propagation[22,23], since the former reaction involves a transition from a more stable to a less stable carbanion.

The influence of the structure of the radical in the organosodium compound on its initiating capacity was studied by Wooding and Higginson[1], who showed that in the majority of cases the latter increased with increase in basicity of the radical.

An interesting feature of polymerisation with organometallic catalysts is the fact that under certain conditions chain growth can continue until the system is completely depleted of monomer. This type of polymerisation without chain termination can be achieved in the absence of chain-terminating impurities, in solvents of low proton-donating capacity, as a result of the relatively low rate of chain transfer for a number of monomers (in comparison with the rate of chain growth). In such systems the molecular weight of the polymers increases with time, and organometallic compounds of very high and comparatively uniform molecular weight, with the alkali metal as an end group, can be obtained[24,25].

The molecular weight is given by the ratio M/c, where M is the amount in grams of monomer which has been polymerised, and c is the number of moles of catalyst.

If on depletion of one monomer another is introduced, so-called block copolymers can be obtained. This peculiarity of organometallic compounds of forming so-called "live" polymers is known in the polymerisation of several monomers with lithium alkyls[26–28] and also in the polymerisation of unsaturated compounds with organosodium compounds[29].

Paul et al.[30] have shown that metallic sodium gives with aromatic hydrocarbons soluble coloured 1 : 1 complexes consisting of a negatively charged aromatic-hydrocarbon ion and the Na^+ ion. The negatively charged hydrocarbon ion of such compounds acts as an electron carrier.

Szwarc and his collaborators[29,31] investigated the polymerisation of various monomers in the presence of complexes of sodium and naphthalene in tetrahydrofuran. It is suggested that in the presence of unsaturated compounds containing conjugated double bonds an electron passes from the naphthalene to the unsaturated compound with formation of the radical–ion $\cdot CH_2-\bar{C}HR$.

At low temperatures they rapidly dimerise, the radicals

* Methods for synthesising these compounds and their properties are described in several monographs[18–20].

recombining and a growing dianion appearing in the system. If polymerisation is carried out with carefully purified reagents (in the absence of moisture or oxygen), the process continues until all the monomer is used up. It has been shown that the molecular weight of the polymers formed is equal to the amount of monomer divided by half the number of moles of catalyst taken (two molecules of catalyst are used in forming a single molecular chain). A similar molecular-weight relationship was observed by Szwarc and his collaborators in the polymerisation of styrene[24], butadiene, and isoprene[31] by means of a sodium–naphthalene complex in tetrahydrofuran. Block copolymers were obtained by successive introduction of different monomers and exhaustive polymerisation of each component.

The kinetics of polymerisation in the presence of alkali metals have been little investigated.

The first studies of the kinetics of anionic polymerisation were made by Abkin and Medvedev[32] on the gas-phase polymerisation of butadiene by metallic sodium. They concluded that this reaction is a catalytic chain process. The rate of polymerisation of butadiene increased as the sodium dissolved, i.e. as it was converted into an organosodium compound. When the metallic sodium was all used up, the process became stationary, and the reaction velocity depended on diffusion of monomer into the polymer, remaining constant after freezing and unfreezing the system and also on successive evacuation and admission of butadiene; this indicates that the anionic process is predominant under these conditions. According to these authors, the activation energy for the polymerisation of butadiene in the presence of metallic sodium is 12 500 kcal/mole.

Owing to the very high rates of polymerisation of monomers by organosodium and organopotassium compounds in the presence of polar additives (ethers, amines) it is difficult to investigate the kinetics of these processes. Mamontova et al.[33] were able to study the kinetics of the polymerisation of butadiene in ethereal solution with α-cumenylpotassium by carrying out the reaction at low concentrations of butadiene (supplied from the gas phase). The activation energy of this process is 7500 kcal/mole.

Kinetic studies of the polymerisation of α-methylstyrene with a sodium–naphthalene complex in tetrahydrofuran were made by Worsfold and Bywater[34]. This process was relatively slow owing to the low reactivity of α-methylstyrene towards anionic polymerisation. The work was carried out at temperatures below 0°, since at higher temperatures depolymerisation of the polymer occurs on a considerable scale. The authors had previously studied the monomer–polymer equilibrium ($P_i + M \rightleftharpoons P_{i+1}$) in this system at various temperatures, and estimated the heat and entropy changes for this reaction[35]: ΔH = 8 kcal/mole and ΔS = = -26.14 cal/mole deg. They showed that depolymerisation is significant only at temperatures above -50°. At -80° no depolymerisation is observed, and the molecular weight of the polymer is given by the relation $M = M/0.5c$. The reaction velocity at temperatures above -50° is given by the equation

$$-\frac{dM}{dt} = kc(M-M_e),$$

where c is the concentration of the sodium–naphthalene complex, M the concentration of monomer at time t, and M_e is the equilibrium concentration of monomer at the given temperature. From the temperature variation the apparent activation energy was estimated as ~ 2–3 kcal/mole.

Polymerisation in the presence of organolithium compounds is very peculiar and will be discussed in a separate section.

III. SPECIAL FEATURES OF POLYMERISATION IN THE PRESENCE OF METALLIC LITHIUM AND ORGANOLITHIUM COMPOUNDS

An interesting feature of polymerisation brought about by organic compounds of the alkali metals is the dependence of the structure of the polymer chain and hence the properties of the resulting polymers on the nature of the catalyst and the medium used.

Yakubchik[36] and Korotkov[37] and their coworkers showed that in the polymerisation of butadiene the proportion of 1,2-structures increases on replacing alkyllithium by alkylsodium and alkylpotassium catalysts.

Using a lithium alkyl, Piotrovskii[38] and Korotkov[37] found that the proportion of 1,2-structures in polybutadiene increases on passing from hydrocarbon solvents to ether and dioxan. Kropachev et al.[39,40] showed that small additions of oxygen, alcohols, phenol, and dialkyl sulphides have a similar effect on the chain structure in the polymerisation of butadiene by organolithium compounds in hydrocarbon solvents.

Tobolsky and Rogers[41] established that the chain structure of polyisoprene, made with the aid of alkali-metal alkyls and aryls, changes according to the nature of the metal and the solvent, but does not depend on the structure of the radical linked to the alkali metal. Table 1 gives some of their data.

TABLE 1. Dependence of the structure of polyisoprene on conditions of polymerisation.

Catalyst	Solvent	1,2, %	3,4, %	cis-1,4, %	trans-1,4, %
n-Butyllithium	n-heptane	0	7	93	0
Lithium	ditto	0	6	94	0
Phenylsodium	»	8	45	0	47
Benzylpotassium	»	10	38	0	52
Lithium	triethylamine	3	45	0	52
n-Butyllithium	tetrahydrofuran	16	54	0	30
Phenylsodium	ditto	13	49	0	38
Sodium	»	15	51	0	34
Benzylpotassium	»	17	40	0	43

Korotkov and his coworkers[37] discovered that the composition of butadiene–styrene copolymers also depends on the nature of the alkali metal and the medium.

An analogous relation between the composition of copolymers and the conditions of polymerisation was observed by Tobolsky et al.[42,43] in the copolymerisation of isoprene with styrene, and by Spirin et al.[28] in the copolymerisation of styrene with α-methylstyrene and of isoprene with butadiene. Relevant data are given in Table 2.

Welch[26] and Spirin et al.[28] have shown that the rate of polymerisation of styrene in the presence of lithium alkyls at concentrations below 0.02 molar in aromatic solvents is

TABLE 2. Dependence of the composition of copolymers on conditions of polymerisation.

M_1	M_2*	Catalyst	Solvent	Initial composition, mole % of M_1	Composition of copolymer, mole % of M_1
Styrene	butadiene	n-butyllithium	heptane	50	5
ditto	ditto	ditto	heptane + ether	50	40
»	»	n-butylsodium	benzene	50	45
»	isoprene	n-butyllithium	benzene	50	14
»	ditto	ditto	tetrahydrofuran	50	72.4
»	α-methylstyrene	ethyllithium	benzene	16.1	79.6
»	ditto	ditto	triethylamine	16.7	96.45
»	»	triphenylmethyl-sodium	benzene + ether	16.7	94.7
Isoprene	butadiene	ethyllithium	benzene	50	24.8
ditto	ditto	ditto	benzene + triethyl-amine	50	14.4
»	»	triphenylmethyl-sodium	benzene + ether	50	13

* M_1 and M_2 represent the monomers undergoing copolymerisation.

proportional to the concentration of monomer and of catalyst. The molecular weight of the polymers increases with increase in the amount of monomer polymerised ("live" polymers) and is given by the ratio M/c, where M is the quantity of monomer in grams, and c is the number of moles of the catalyst. At concentrations > 0.02 molar, the reaction velocity is independent of the concentration of lithium alkyl, which is explained by association between the catalyst molecules[44,45] at these concentrations.

In the polymerisation of isoprene under similar conditions, Korotkov et al.[46] have shown that the reaction velocity is independent of the concentration of lithium alkyl at considerably lower concentrations of the latter, possibly owing to the formation of more stable association complexes in this system. The formation of "live" polymers of isoprene and butadiene has been observed by Korotkov et al.[27] when these monomers are polymerised by butyllithium. Increase in the molecular weight with the amount polymerised occurs in the methyl methacrylate–butyllithium system at low temperatures[47].

Data on the kinetics of the polymerisation of styrene show that, after a short initial period, the rate of polymerisation is equal to the rate of chain growth[26,28].

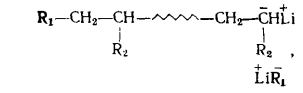
According to Welch[26] and to Spirin et al.[28], the activation energy for chain growth in the polymerisation of styrene by lithium alkyls in a hydrocarbon medium is 17 and 16 kcal/mole, and the frequency factors are 10^{11} and 5×10^{11} litres/mole sec respectively. The rate of polymerisation increases sharply on addition of diethyl ether, tetrahydrofuran, and triethylamine, the greatest effect being exerted by tetrahydrofuran. However, the rate of polymerisation is considerably lower in the presence of lithium alkyls than in the presence of sodium alkyls under the same conditions.

Korotkov[37] and O'Driscoll and Tobolsky[48] concluded from the results that one molecule of ethyllithium is coordinated with two molecules of ether or tetrahydrofuran. On adding ether the reaction velocity increased with increase in its concentration even when a very large excess relative to the catalyst was present[37].

According to Spirin et al.[28], with a triethylamine : catalyst ratio > 20, the rate of polymerisation of styrene is independent of the concentration of the amine. Under these conditions also the molecular weight is given by the ratio M/c, the activation energy and the frequency factor being 13.6 kcal/mole and 6.2×10^{10} litres/mole sec respectively. Comparison of data on the polymerisation of styrene in the presence and absence of triethylamine shows that the increase in the rate caused by its presence is due to a reduction in the activation energy.

α-Methylstyrene has been found to polymerise in the presence of a lithium alkyl[28] as well as with a sodium–naphthalene complex[35]. Owing to the relatively low limiting temperature of polymerisation for this monomer, appreciable yields of polymer can be obtained only by lowering the temperature and increasing the concentration of the monomer[49]. Whereas addition of butadiene diminished the rate of polymerisation of styrene and isoprene in hydrocarbon solvents[37,50], addition of α-methylstyrene to styrene had practically no effect on the reaction velocity[28].

The above facts show that the structure of the polymer chain formed in the separate polymerisation of dienes and in copolymerisation of certain monomers in the presence of a lithium alkyl differs markedly from the structure obtained when organosodium and organopotassium compounds in polar solvents are used. Korotkov and Tobolsky have pointed out that the observed effect is due to the differing polarities of the M–R bond in the organometallic compounds. Mark[51] considers that during polymerisation with organolithium compounds the tip of the growing chain is an ionic quadrupole:



which forms a complex with the monomer and controls the addition of monomer to the growing chain.

Spirin et al.[28] have suggested the following way of regarding the influence of the alkali metal on the structure of the chain. With a typically anionic mechanism (e.g. NaR in an ether) chain growth is determined by reaction of the monomer with a carbanion, and the reactivity of the monomer is determined solely by its electron-acceptor properties. In the series LiR, NaR, KR, the least polar bond is in LiR. These authors suggest that in the presence of LiR reaction of monomer with catalyst is determined both by the electron-donor properties of the R group and by the electron-acceptor properties of the lithium component of the catalyst. The participation of the lithium component in chain growth can occur by the formation of π-complexes with monomers, which polarise the LiR bond. (Because of the relatively feeble electron-acceptor properties of the lithium component of the catalyst[37], only a small proportion of the catalyst is combined as a π-complex with the monomer.) Chain growth then occurs according to the scheme

$$M + LiM_nR \rightarrow M : LiM_nR,$$
$$M{:}LiM_nR \rightarrow LiM_{n+1}R.$$

Spirin et al. also consider it possible that chain growth occurs by a single-stage reaction with simultaneous reaction of a monomer molecule with the lithium and the carbanion component of the catalyst. In this case the transition state is a four-membered ring in the polymerisation of olefins and a six-membered ring in the polymerisation of dienes.

The data of Lyudvig et al.[52] on the kinetics of cationic

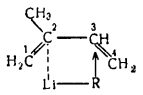
polymerisation show that the ability of monomers to react with electron-acceptors increases with increase in the electron density at the double bond: α-methylstyrene > > isoprene > butadiene > styrene.

Since with an LiR catalyst chain growth is due to reaction of monomer not only with the carbanion but also with the lithium component of the catalyst (an electron-acceptor), the composition of copolymers obtained in the presence of LiR should be different from that produced by a typical carbanion mechanism, in which chain growth is due solely to reaction between monomer and carbanion. This effect is particularly marked when one of the two monomers contains two conjugated double bonds, one of which reacts preferentially with the lithium and the other with the carbanion component of the catalyst.

Spirin et al.[28] point out that to assess the relative reactivities of monomers in a typically anionic polymerisation it is necessary to study copolymerisation brought about by organosodium, organopotassium, or organolithium compounds in the presence of additives with strong electron-donor properties. The above treatment enables the authors to explain the predominance of the *cis*-form in polyisoprene obtained by polymerisation with organolithium compounds in hydrocarbons.

In the polymerisation of isoprene by radical[53] and cationic[53,54] mechanisms a polyisoprene is obtained with a predominantly *trans*-1,4-structure; under conditions typical of an anionic mechanism (NaR + ether)[41] a polyisoprene with a predominantly *trans*-1,4 and *trans*-3,4 form of addition is obtained. It may be assumed that with 1,4-addition, the *trans*-structure corresponds to a lower activation energy than the *cis*-form in all three mechanisms*. This hypothesis is supported by data on the radical polymerisation of isoprene[53], according to which the proportion of the *cis*-structure increases with rise in temperature.

In the presence of LiR the 1,2-double bond of isoprene, which possesses a greater electron density, will react preferentially with the lithium component of the catalyst, and the carbanion component R will react with a fourth carbon atom of the isoprene molecule, so that the spatial arrangement will be most favourable to *cis* addition:



An analogous mechanism for producing polyisoprene with a predominantly *cis*-1,4 mode of addition was suggested by Gaylord and Mark[54] for the polymerisation of isoprene with lithium and organolithium compounds in a hydrocarbon medium. They suggest that in order to obtain *cis*-1,4-polyisoprene the process must be carried out under hetereogeneous conditions.

It is also possible that polymerisation with combined catalysts of the Ziegler–Natta type does not take place by a typically anionic mechanism, but the monomer molecule reacts simultaneously with the two components of the complex catalyst, leading to a selective orientation of the monomers and a stereospecific polymerisation.

* The fact that *trans*-1,4-addition by three different mechanisms evidently has a lower activation energy is probably associated with a greater heat of reaction for this structure, and hence, in conformity with Polanyi's rule[55], a lower activation energy.

IV. POLYMERISATION IN THE PRESENCE OF ALFIN CATALYSTS

While investigating the polymerisation of monomers with alkali-metal alkyls and aryls, Morton et al.[56] found that a combined catalyst consisting of a sodium alkyl, alkoxide, and salt is very active in the polymerisation of butadiene and other unsaturated molecules. Particularly interesting results were obtained with allylsodium associated with sodium isopropoxide and chloride, the so-called "Alfin"* catalyst, which is insoluble in hydrocarbons and is used in the form of dispersions in hydrocarbon media. It was shown that in such systems polymerisation occurs only on the surface of the catalyst, the homogeneous solution being inactive.

Replacement of allylsodium by an Alfin catalyst greatly increased the rate of polymerisation of butadiene (~ 50–60 times) and also the molecular weight of the resulting polymer (from 100 000 to 7 000 000). The number of terminal double bonds was diminished (from 60 to 20%), and a polybutadiene with a predominantly *trans*-1,4 mode of addition was obtained. A similar, but less marked, increase in reaction velocity and molecular weight was observed on passing from sodium alkyls to an Alfin catalyst in the polymerisation of styrene[57]; a smaller effect was observed in the polymerisation of isoprene.

In a later paper Morton and Ward[58] showed that when butadiene is polymerised with pentylsodium additions of triethylamine and caustic soda also cause a sharp increase in the *trans*-1,4 mode of addition (from 23 to 64%).

Williams et al.[59,60] found that the polystyrene resulting from polymerisation of styrene with an Alfin catalyst has a regular structure, and passes into a highly crystalline polymer on heating in various solvents. When the process was carried out with an Alfin catalyst in polar solvents — diethyl ether, dioxan, pyridine — the rate of polymerisation was increased, and an amorphous polystyrene of irregular structure was obtained. The catalyst was inactivated by prolonged contact with ether. These workers suppose that the change in the structure of polystyrene and the increase in activity of the catalyst in the presence of polar solvents are due to the formation of complexes between solvent molecules and sodium ions at the surface of the catalyst, which accelerate polymerisation and prevent the selective orientation of the monomer.

At the present time very few quantitative data are available on the mechanism of polymerisation in the presence of Alfin catalysts.

Morton[61] suggests that polymerisation in the presence of Alfin catalysts occurs by adsorption of the reactants on an ionic aggregate with coordination and activation of the monomer molecule at the surface, followed by its reaction with an anion located on the surface. Study of the influence of the physical parameters of the components which affect the surface properties of the catalyst showed[62] that the nature of the alkali metal and the anion of the inorganic salt have a substantial effect on the activity of the catalyst. Among inorganic alkali-metal salts those are active in which the sum of the ionic radii d is greater than 2.75 Å.

* The name "Alfin" arose in the early stages of the investigation when it was supposed that only two components — a sodium alkoxide and an olefin — were required to produce this catalyst. Further work showed that a third component — an inorganic salt — is necessary.

Thus NaCl (d = 2.81 Å) can be replaced by KCl (3.14 Å), but its replacement by LiCl (2.57 Å) markedly diminishes the activity of the catalyst. When lithium chloride is replaced by lithium iodide (3.02 Å), the catalyst exhibits considerable activity.

Much is still obscure in the mode of action of Alfin catalysts. However, the nature of the catalyst and the observed behaviour support an anionic mechanism of polymerisation in these systems.

Korotkov[37] investigated the copolymerisation of several pairs of monomers by Alfin catalysts and showed that the composition of the resulting copolymers was close to that characteristic of anionic polymerisation. The observed activity series of the monomers in individual Alfin polymerisations — butadiene > styrene > isoprene — is the same as that for the reactivity of these monomers in copolymerisation with Alfin[37] and anionic catalysts (see Part VII). The specific features of Alfin polymerisation, as compared with polymerisation by alkali-metal alkyls and aryls in hydrocarbon solvents, can be explained by the following factors: (1) the presence of polar additives (sodium isopropoxide, sodium chloride), which polarise the Na–R bond and thus sharply accelerate polymerisation, and (2) the insolubility of the associated ionic aggregate of the catalyst in the hydrocarbon solvent, which governs the selective orientation of monomer at the catalyst surface.

As pointed out above (Part II), very high polymerisation rates were also observed in the presence of sodium alkyls with polar additives.

The high molecular weights of Alfin polymers is evidently connected with the characteristic ability of anionic polymers to form "live" polymers (see Part II); in conjunction with the high reaction rates produced by polar additives and the small number of active centres (only surface complexes are effective), this may be the reason why products of very high molecular weight are formed after a short period of polymerisation.

V. SIMULTANEOUS ANIONIC AND RADICAL POLYMERISATION IN THE PRESENCE OF ALKALI METALS

Several investigations have shown that formation of a radical-ion by reaction of an alkali metal with an unsaturated molecule does not always lead solely to anionic polymerisation. In a number of cases the competing radical polymerisation predominates, and sometimes the two processes occur simultaneously.

Overberger et al.[63] found the rate of polymerisation of methacrylonitrile in liquid ammonia to be considerably greater with lithium than with lithium amide, and the laws governing the process were also different. Thus, for example, with lithium amide the molecular weight was independent of the catalyst concentration, whereas with lithium itself the molecular weight fell with increasing concentration of catalyst. These workers assume that lithium reacts with the monomer to form a radical-ion:

$$Li + CH_2{=}CHR \rightarrow \cdot CH_2{-}\bar{C}HR\overset{+}{L}i.$$

Comparison of the rates of polymerisation in the two systems, containing lithium and its amide, lead to the conclusion that radical polymerisation predominates in the reaction of lithium with methacrylonitrile in liquid ammonia. The dependence of the molecular weight on the catalyst concentration also suggests a radical mechanism in this system. O'Driscoll et al.[64,65], from the composition and properties of styrene–methyl methacrylate copolymers formed in the presence of metallic lithium, also concluded that two competing processes, radical and anionic, are occurring. At lower temperatures the anionic polymerisation predominates; this is explained by a sharper change in the velocity of radical polymerisation with temperature.

In the polymerisation of isoprene in a hydrocarbon medium with a dispersion of lithium anionic polymerisation, by the organolithium compounds formed, evidently occurs preferentially and the proportion of radical polymerisation is small, since under these conditions the polyisoprene obtained has a predominantly *cis*-1,4-structure (96%)[66] (see Part III).

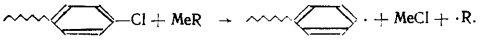
Hirota et al.[67] used a paramagnetic-resonance method to detect the presence of radicals during the polymerisation of styrene in the presence of metallic sodium. They consider that a radical-ion,

$$\cdot CH_2{-}\underset{\displaystyle R}{\bar{C}H}{-}\overset{+}{N}a$$

is formed, and that both radical and anionic polymerisation occur.

On passing to polar solvents, or in the presence of monomers containing polar groups, only anionic polymerisation is observed with metallic sodium. Thus, for example, copolymers of styrene and methyl methacrylate obtained with metallic sodium and with triphenylmethylsodium have the same composition[68].

Spirin et al.[23], studying the copolymerisation of styrene with *p*-chlorostyrene in the presence of various organometallic compounds, also observed the presence of two competing reactions, anionic and radical polymerisation. Radicals were formed in this system by the interaction of the organometallic compound with the *p*-chlorostyrene by a Wurtz type of reaction:



Either radical or anionic polymerisation predominated depending on the experimental conditions. The former predominated in the presence of ethyllithium in a hydrocarbon medium, and the latter with organolithium and organosodium compounds in the presence of triethylamine.

The kinetics of polymerisation of styrene with ethyllithium show that after a short initial period all the ethyllithium molecules have been transformed into organometallic compounds of lithium with polystyrene, which form the active centres of growth. In the absence of chain-terminating impurities, these compounds become "live" polymers. When *p*-chlorostyrene is present, it reacts with the lithium compound to produce chain termination and formation of free radicals. Owing to the relatively low reactivity of the chlorine atom in the benzene ring, this reaction is slow. The number of radicals formed in the system from the start of the reaction until the catalyst has been completely decomposed is double the original number of active centres, i.e. of carbanions formed from the ethyllithium.

Data relating to the rates of chain growth in the polymerisation of styrene by a radical mechanism and with an ethyllithium catalyst at 30° are given in Table 3. They show that the rate of chain propagation is greater for the radical polymerisation of styrene than for its polymerisation with ethyllithium even in an amine medium.

TABLE 3. Velocity constants for chain growth in the polymerisation of styrene by a radical mechanism and with an ethyllithium catalyst.

Catalyst	Solvent	Rate, moles litres^{-1} sec^{-1}	Reference
Benzoyl peroxide	—	53	69
Ethyllithium	toluene	0.131	28
ditto	toluene + triethylamine	8.5	28

Data on copolymerisation show that the rates of chain growth in the radical polymerisation of styrene and of *p*-chlorostyrene are similar[70]; when polymerisation is carried out with the aid of ethyllithium in an amine medium the relative reactivity of *p*-chlorostyrene is six times as great as that of styrene itself[23]. Combination of these results with the data in Table 3 shows that rates of chain growth for *p*-chlorostyrene are similar for radical polymerisation and in the presence of ethyllithium together with an amine. Nevertheless, anionic polymerisation predominated in the copolymerisation of *p*-chlorostyrene with styrene in the presence of ethyllithium and an amine, obviously because of the considerably longer life of an anionic active centre compared with a radical one. In polymerisation with ethyllithium in a hydrocarbon medium, radical polymerisation predominated in spite of the shorter life of a radical active centre, since under these conditions the rate of chain growth by an anionic mechanism is 400 times lower than by a radical mechanism.

VI. PREPARATION OF POLYMERS OF REGULAR STRUCTURE BY ANIONIC POLYMERISATION

During recent years there has been a considerable expansion of work on the synthesis of polymers of regular structure, the so-called isotactic and syndiotactic polymers. Crystalline polymers, corresponding to polymer chains of isotactic and syndiotactic structures, usually differ markedly in physical and mechanical properties from the corresponding atactic amorphous polymers.

With polymers of the diene series, the presence of a double bond in each structural unit makes possible, in addition to these types of polymers of regular structure, the existence of *cis*- and *trans*-isomers with the 1,4-structure, produced by different arrangements of the first and fourth carbon atoms of the monomer unit relative to the double bond.

In the development of work on the preparation of stereoregular polymers with combined Ziegler–Natta catalysts the insolubility of the catalyst in the hydrocarbon solvents generally employed has led to the quite widely held view that stereospecific polymerisation can occur only in the presence of an orienting surface in heterogeneous systems. Several investigators have shown, however, that isotactic and syndiotactic polymers can also be obtained under homogeneous conditions and not only by ionic but also by radical polymerisation[71].

In 1944 Huggins[72] noted that in the homogeneous polymerisation of vinyl monomers different types of addition of the monomers may be expected in chain-growth reactions, distinguished by the distribution of the substituents H and R relative to the plane of the C–C bonds in the main chain; by varying the conditions of polymerisation it is possible to achieve the predominance of one of the possible arrangements.

Fox et al.[71] and also Colleman[73] made a statistical analysis of the conditions leading to the formation of polymers of one structure or the other. Their basic idea was that any polymer could be regarded as a copolymer consisting of isotactic and syndiotactic groups and that the two types of addition might have different energies and entropies of activation. From the statistical analysis they obtained an expression for the probability of an isotactic or a syndiotactic chain structure as a function of the differences in energies and entropies of activation. Knowing the magnitudes of these differences, it was possible to estimate in what temperature range one or other structure would predominate.

Thus both this general discussion and direct experimental results indicate that stereoregular polymers can be obtained not only under heterogeneous but also under homogeneous conditions.

With anionic polymerisation, polymers of regular structure have been obtained both in heterogeneous systems and in a homogeneous medium. As already mentioned, lithium alkyls in a hydrocarbon solvent give a polyisoprene mainly with a *cis*-1,4 mode of addition. Isotactic and syndiotactic poly(methyl methacrylate) and isotactic polystyrene have also been obtained by anionic polymerisation. Fox et al.[74] have shown that isotactic poly(methyl methacrylate) is formed by homogeneous polymerisation of methyl methacrylate with organic compounds of lithium in toluene at low temperatures, owing to the orienting influence of the lithium component of the catalyst on chain propagation. Isotactic poly(isopropyl and cyclohexyl acrylates) have been obtained under similar conditions[75]. In the presence of the polar solvent 1,2-dimethoxyethane syndiotactic poly(methyl methacrylate) is formed. The structure of this polymer was established by Stroupe and Hughes[76].

Miller et al. obtained a highly crystalline poly(t-butyl acrylate) by polymerisation with a dispersion of lithium[77], and a crystalline poly(methyl methacrylate) by carrying out polymerisation in the presence of a Grignard reagent[78]. By varying the conditions of polymerisation they also obtained isotactic and syndiotactic poly(methyl methacrylate). Crystalline polystyrene was obtained with organopotassium[79] and organosodium[80] compounds in hexane, and also with an Alfin catalyst[59,60], i.e. in systems containing the catalyst in suspension.

Polymers of regular structure have thus been obtained by anionic polymerisation under homogeneous conditions only in the presence of organolithium compounds, as a result of the orienting influence of the lithium component, which takes part, together with the carbanion component of the catalyst, in the chain growth process*.

VII. ANIONIC COPOLYMERISATION

Copolymerisation is widely used for the synthesis of polymers with valuable properties. Apart from the

* These polymers are formed only from those monomers which contain at least two functional groups, one of which reacts with the lithium and the other with the carbanion component of the catalyst, resulting in the selective orientation of the monomer unit.

TABLE 4. Composition of styrene – methyl methacrylate copolymers obtained by different mechanisms of polymerisation. (Initial molar ratio 1 : 1).

Catalyst	Composition of copolymer, mole % of styrene	Mechanism of polymerisation
BF_3 etherate	99	cationic
Benzoyl peroxide	51	radical
Triphenylmethylsodium	~1	anionic

TABLE 5. Copolymerisation constants for different pairs of monomers in the presence of alkali metals and their compounds as catalysts.

Monomers M_1	Monomers M_2*	Catalyst	Solvent	r_1	r_2**	Reference
Isoprene	butadiene	butyllithium	hexane	0.47	3.38	50
»	diisopropenyl	»	»	17	0.06	85
»	piperylene	»	»	17	0.06	85
»	»	»	hexane + ether	5	—	85
Methyl methacrylate	styrene	sodium	liquid ammonia	6.4	0.12	86
ditto	methacrylonitrile	sodamide	ditto	0.61	5.2	87
»	acrylonitrile	»	»	0.25	7.9	88
»	methyl acrylate	»	»	0.1	4.5	88
»	vinyl acetate	»	»	3.2	0.4	88
Acrylonitrile	butyl vinyl sulphone	»	»	1.1	0.2	89
p-Chlorostyrene	styrene	ethyllithium	benzene + triethylamine	6.5	0.1	23

* M_1 and M_2 represent the monomers undergoing copolymerisation.

** r_1 and r_2 are copolymerisation constants.

practical value of this method, it is a useful source of information about the relative reactivities of monomers and hence the nature of the active centres, which is particularly important in the application of new catalysts.

The composition of several copolymers differs markedly according as the process occurs by a cationic, an anionic, or a radical mechanism. Among these must be mentioned the styrene–methyl methacrylate system, which is frequently employed by investigators to determine the mechanism of polymerisation. The compositions of copolymers of this system for radical, cationic, and anionic polymerisation are given in Table 4 [68,81].

In an investigation of some new catalysts — cadmium alkyls [82], boron alkyls [83], and $CaZn(C_2H_5)_4$ [84] — the composition of the products showed that a radical mechanism was operative with the first two catalysts, and that anionic polymerisation took place with the third.

Copolymerisation constants for several pairs of monomers in the presence of alkaline catalysts are given in Table 5.

The copolymerisation constants obtained for the isoprene–butadiene, isoprene–diisopropenyl, and isoprene–piperylene systems with a butyllithium catalyst in a hydrocarbon medium do not indicate the relative reactivities of these monomers when undergoing polymerisation by a carbanion mechanism (see Part III). If ether [85] or triethylamine [28] is added, i.e. with carbanion polymerisation, the content of butadiene and piperylene in the copolymer is greater than in that obtained with organolithium compounds in a hydrocarbon medium [28,50,85].

All the remaining systems in Table 5 were studied in polar solvents, and the corresponding copolymerisation constants are a measure of the relative reactivities of the monomers in carbanion polymerisation.

From the data in Table 5 and Part III the monomers can be arranged in the following order of relative reactivity: acrylonitrile > butyl vinyl sulphone > methyl acrylate > > methacrylonitrile > methyl methacrylate, *p*-chlorostyrene > vinyl acetate > butadiene > styrene > isoprene > α-methylstyrene.

As already mentioned, an interesting feature of anionic polymerisation is that in several cases the rate of polymerisation is equal to the rate of chain growth. For these systems the rate constants for chain growth can be obtained directly from kinetic data. Combination of these data with the copolymerisation constants for these monomers with another monomer, the same in all cases, enables us to estimate in the usual way [90] the relative reactivities of carbanions of different structure towards the given monomer.

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With regard to anionic polymerisation, little quantitative information is yet available on how the reactivity of catalysts, monomers, and the corresponding carbanions depends on their structures, or on how the conditions of polymerisation affect the structure and properties of the polymers formed.

The quantitative study of these systems is difficult since conditions of great purity are necessary — traces of oxygen, moisture, sulphur compounds, or other impurities which react with the catalyst and the carbanion, must be absent.

Furthermore, the rate of polymerisation in anionic systems is often so great (e.g. the polymerisation of styrene with a sodium–naphthalene complex in tetrahydrofuran) that accurate kinetic measurements are impossible by the dilatometric method, which is widely used to measure rates of polymerisation. Other methods are required to determine the velocity constants for chain propagation in such systems.

The development of this work should lead to wider and more quantitative information about the mechanism of these very unusual and practically valuable processes.

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CATALYTIC HYDROGENATION OF PHENOLS

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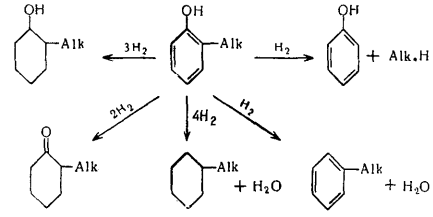
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INTRODUCTION

The primary tar obtained on processing a solid fuel contains a considerable quantity of phenols. Phenol itself and, to some extent, the cresols, are widely employed in industry for the preparation of plastics, synthetic fibres, dyes, chemical insecticides, anti-oxidants, tanning agents, varnish resins, etc. However, xylenols and other higher phenols have so far been insufficiently utilised. Any widespread use of these phenols is prevented by the absence of satisfactory methods for isolating them from the primary tar and for separating them. For this reason, besides the investigation of ways of effectively utilising individual phenols, efforts have been directed towards finding a method of converting the separate fractions of the primary tar into chemical products of value to the economy without isolating the individual components. A hydrogenation treatment is of great importance for exploiting phenols in this way, as it allows either phenol and cresols or hydrocarbons to be obtained from the higher phenols. Hydrogenation has now achieved wide application not only in laboratory practice but also in industry. The hydrogenation of coal, the reductive cracking of petroleum products, and also the refining and stabilisation of crude fuel have been extensively developed.

The hydrogenation of phenols can produce several types of changes: (1) hydrogenation of the benzene ring with retention of the hydroxyl group; (2) hydrogenation to hydroaromatic ketones; (3) conversion of phenols into aromatic and alicyclic hydrocarbons; and (4) reductive dealkylation of higher phenols with the formation of lower phenols:



In a review of published results it is convenient to separate these types of reactions. A description of earlier work on the changes undergone by phenols on hydrogenation has been given by Sabatier[1], Ellis[2], as well as in papers by Tishchenko and Belopol'skii[3], Petrick[4], Moldavskii and Lifshits[5,6] and Rapoport[7], and in the monograph by Lozovoi and D'yakova[8].

The literature on the hydrogenation of phenols is quite extensive. The majority of papers, however, are concerned with the hydrogenation of phenol itself, cresols, and to some extent xylenols. The behaviour of the higher phenols under conditions of hydrogenation has been quite inadequately studied. Investigation of the catalytic changes undergone by the higher fractions of the primary tar, both under conditions of hydrogenation and during processes of alkylation and dealkylation, is necessary for the successful solution of the problem of the effective utilisation of primary tars. It is therefore useful to investigate catalytic changes which occur on hydrogenation, both of the individual phenols in the higher fractions of the primary tars, and of narrow fractions in which one or other component has been concentrated. These fractions can be isolated by fractionation and chromatography. Up to the present, unfortunately, too little attention has been paid to these methods.

I. HYDROGENATION OF PHENOLS TO HYDROAROMATIC ALCOHOLS

The hydrogenation of phenol was first accomplished by Sabatier and Senderens in 1903 by passing phenol vapour together with excess hydrogen over reduced nickel at 215°–230°.[1] The main product was cyclohexanol mixed with cyclohexanone and small quantities of cyclohexene, cyclohexane, and benzene. At highter temperatures (250°–

300°) hydrogenation of the phenol nucleus did not occur at all, but partial reduction of phenol to benzene was observed. The hydrogenation of cresols and xylenols was also investigated. The latter, on hydrogenation by the Sabatier method, behave in various ways: 2,4-xylenol at 190°–200° gives the corresponding alicyclic alcohol in good yield; when 2,5-xylenol is hydrogenated, the hydroaromatic alcohol is accompanied by up to 10% of the cyclic ketone. In contrast, the main product of the hydrogenation of 3,4-xylenol under the same conditions is *o*-xylene (67%), only 25% of dimethylcyclohexanol and 8% of the ketone being obtained.

In 1906 Ipat'ev[9,10] first accomplished the hydrogenation of phenol in the liquid phase, in the presence of nickel oxide under a high pressure of hydrogen in a bomb at elevated temperatures. At 104 atm and 238° for 55.5 h he obtained pure cyclohexanol; lowering the temperature of hydrogenation to 215°–220° led to the formation of a mixture of cyclohexanol and cyclohexanone. These results were later reproduced by Osterberg and Kendall[11]. Orlov et al.[12] showed that the amount of catalyst taken was of great significance in liquid-phase hydrogenation by Ipat'ev's method; thus decreasing the amount of nickel oxide from 8 to 0.4% of the phenol taken trebles the time required for the reaction.

It was subsequently found that higher temperatures and pressures are not necessary to obtain homologues of cyclohexanol by the hydrogenation of phenols. Brochet[13] showed that hydrogenation of the cyclic double bonds in the phenol has already begun at 50°, and is complete between 100° and 120°. He obtained high yields of cyclohexanol, without admixture of the ketone, cyclohexene, or cyclohexane, with three specimens of reduced nickel (nickel vif, nickel carbonique, and nickel formique) at 130°–150° and an initial pressure of 10–15 atm in a copper autoclave. Similar results were obtained by Tishchenko and Belopol'skii, working with analogous conditions[13]. Raising the hydrogen pressure increases the rate of hydrogenation of phenol, but only up to a certain limit[14].

The production of hydroaromatic alcohols from phenols has been investigated in the presence of various hydrogenation catalysts — platinum, palladium, copper, and nickel.

Hydrogenation of phenol in the presence of copper catalysts was unsatisfactory. Thus over reduced copper at 200°–230° and 80 atm only 58% of cyclohexanol was obtained together with 10% of cyclohexane and 3% of dicyclohexyl ether[15]. A mixed copper–nickel catalyst gave somewhat better results, but only with liquid-phase hydrogenation; hydrogenation in the vapour phase was very slow and yielded a mixture of products, containing, apart from cyclohexanol, 9–14% of cyclohexanone and not less than 2–3% of high-boiling products, among which dicyclohexylcyclohexanone could be identified[16]. Catalysts based on copper can be conveniently employed for the selective hydrogenation of arylphenols. Thus, for example, in the presence of a copper–chromium catalyst *p*-phenylphenol yields phenylcyclohexanol, whereas in the presence of a chromium–nickel catalyst cyclohexylcyclohexanol is obtained[17].

Nickel catalysts, thanks to their high activity, comparatively low cost, availability, and simplicity of preparation, have been widely used and have now displaced all other catalysts. They are employed mainly in the form of Raney nickel (predominantly in laboratory practice), as an alloy of nickel with aluminium, and in the form of the finely dispersed metal deposited on different carriers. During recent years Japanese investigators have strongly recommended for the hydrogenation of phenols and other organic compounds the use of a nickel catalyst obtained from nickel formate and distinguished, according to their data, by particularly high activity[18,19].

Palfray[20] found that the ease of hydrogenation of the three isomeric cresols decreased in the order $o > p > m$, the times required for hydrogenation in the presence of Raney nickel at 95° and 120 atm and the yields of the corresponding alicyclic alcohols being 90 min and 90%, 160 min and 81%, and 244 min and 68% respectively. Raising the temperature to 250° favoured the formation of methylcyclohexane, especially in the experiments with *m*-cresol. 2,5-Xylenol and 3,4-xylenol were also hydrogenated comparatively slowly.

In addition to the alicyclic alcohol, hydrocarbons were present among the reaction products. *m*-Cresol was hydrogenated in absolute ethanol or methanol in the presence of Raney nickel at 150° and 140 atm to form 3-methylcyclohexanol in high yield[21]; 2- and 4-methylcyclohexanols were obtained in good yield by the hydrogenation of *o*- and *p*-cresols at 150° and 180 atm in the absence of solvent[22].

Nickel catalysts deposited on carriers, mainly keiselguhr and aluminium oxide, have been widely used for the hydrogenation of phenols because of their high and stable activity, and also the ease with which they can be regenerated, which enables the process to be carried out continuously. The regeneration of catalysts is carried out by oxidation with air at 300°–350° followed by reduction, or by some other suitable method[23,24]. Yukhnovskii and Sorokin[25] hydrogenated *o*-, *m*-, and *p*-cresols at 170°–180° and 15–20 atm in the presence of nickel deposited on kieselguhr and with a mixed cobalt–nickel–copper catalyst, and obtained the corresponding methylcyclohexanols in good yield. In the presence of nickel on kieselguhr at 160° and a maximum pressure of hydrogen of 126 atm, *m*-cresol is quantitatively hydrogenated to 3-methylcyclohexanol[26]; hydrogenation of *m*-cresol at atmospheric pressure, 125°–130°, and a volume flow of 0.1–0.2 h^{-1} in the presence of a 10% nickel–alumina catalyst gives 3-methylcyclohexanol in 86% yield, the catalyst not requiring regeneration for quite a long time[27]. 3,4-Dimethylcyclohexanol was the sole product of the hydrogenation of 3,4-xylenol at 100° and 100 atm pressure of hydrogen in the presence of a 20% nickel–alumina catalyst[28]. The catalyst lost its selective action only at temperatures above 250°.[28,29] Cornubert et al.[30] obtained a mixture of isomeric 3,5-dimethylcyclohexanols in 87% yield on hydrogenating 3,5-xylenol by Skita's method[31] in the presence of nickel deposited on kieselguhr. Nickel catalysts, as well as platinum and palladium, are recommended in several patents on the hydrogenation of mono- and di-t-alkylphenols to the corresponding alcohols, which are of interest as intermediates for organic synthesis, insecticides, and anti-oxidants for mineral oils and petrol[32–35]. Hydrogenation of alkylphenols containing seven or more carbon atoms in the alkyl group[36], and also of t-butylphenols[37,38], is carried out in the presence of nickel on kieselguhr. The hydrogenation of alkylphenols having a side chain containing more than five carbon atoms, and of those with tertiary alkyl groups, is complicated by their hydrogenolysis. This can be prevented by carrying out the hydrogenation in the presence of organic bases (pyridine, triethylamine, etc.). In the presence of pyridine, alkylphenols with a side chain containing 9–12 carbon atoms are readily hydrogenated, over nickel on kieselguhr at 250°, giving good yields of the corresponding alkylcyclohexanols, whereas in the absence of pyridine these alkylphenols are completely reduced to hydrocarbons[39].

Nickel catalysts are successfully employed for the hydrogenation of phenols both in the liquid and in the vapour phase in dynamic systems. For vapour-phase hydrogenation at atmospheric pressure d'Or and Orzéchowski[40-42] and Griffith and Hill[43] recommend the use of a nickel catalyst promoted with cerium. In several patents nickel catalysts are recommended for the hydrogenation of phenols by a continuous process both in the liquid phase with a finely dispersed catalyst[44] and in the vapour phase at atmospheric or a somewhat higher pressure of hydrogen[45,46].

According to results obtained by Ungnade and Nightingale[47], promotion of a nickel catalyst with alkali has a favourable influence on the hydrogenation of phenols. In the presence of small amounts of alkali or the corresponding sodium or potassium phenate, phenol and its alkyl derivatives (cresols, xylenols, trimethylphenols, t-butylphenols) are hydrogenated more rapidly and at lower temperatures. Addition of alkali is particularly necessary for the hydrogenation of sterically hindered phenols, in particular 2,6-disubstituted phenols[48]. This might be explained by the intermediate product, the alicyclic ketone, being more readily enolised in the presence of alkali, and the enol form in turn being considerably more readily reduced by the hydrogen. The promoting effect of alkali on the reduction of aldehydes and ketones has been noted also by other authors[49,50]. Paty[51], however, is inclined to explain the activation of the Raney nickel–aluminium catalyst by alkali in terms of the effect of the latter on a nickel–aluminium alloy, leading to a change in the activity of the catalyst.

Tsutsumi et al.[52] have also shown that cresols are more efficiently hydrogenated in the presence of a Raney nickel catalyst if the amount of alkali used is sufficient to dissolve the whole of the aluminium contained in the catalyst.

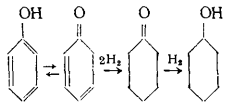
Thus, hydrogenation of the pure individual phenols to hydroaromatic alcohols can be readily achieved at a comparatively low temperature (down to 200°) at high and at ordinary pressures in the presence of nickel or catalysts of the platinum group. Hydrogenation of technical phenolic mixtures is a more difficult problem, owing to the poisoning of the catalyst by sulphur compounds[25,53]. This question has been insufficiently discussed in the literature, and mainly only in relation to the production of cyclohexanol from technical phenol.

Belotzerkovskii[54] noted that a catalyst prepared by heating nickel nitrate to 200° and then reducing it with hydrogen, hydrogenates technical phenol in the vapour phase at 175°–180° provided no thiophenes are present.

Polozov[55] investigated the properties of a series of catalysts not subject to poisoning with sulphur (MoO_3 + + CoS, MoS_3, MoS_3 + S, and $NiMoO_4$) with the aim of obtaining cyclohexanol from technical phenol, and concluded that these catalysts are suitable for hydrogenation only at temperatures of about 220° and above; however, their dehydrating power becomes manifest under these conditions, and diminishes the yield of alcohol.

Rapoport and Sil'chenko[56] achieve a high yield of cyclohexanol (90–95%) from technical phenol in the presence of Raney-type nickel–aluminium and nickel–cobalt–aluminium catalysts at 173°–200° and 50–100 atm pressure of hydrogen. A nickel–aluminium alloy catalyst was first used for the hydrogenation of phenol by Bag et al.[57] Deryabin and Yasnyi[58] obtained 90–95% of cyclohexanol, 3–6% of the ketone, and 0.5–1.0% of cyclohexane by hydrogenating phenol at 130°–140° and 1.5–2.0 atm in the presence of a Bag catalyst. Rapoport and Sil'chenko, by raising the hydrogen pressure during hydrogenation to 50–100 atm, considerably shortened the duration of the process. Supported nickel catalysts, after they have first been specially treated with hydrogen sulphide, may also be useful for the hydrogenation of phenolic tars.

Much research on the hydrogenation of phenols to alicyclic alcohols has been devoted to determining the mechanism of hydrogenation and the configuration of the resulting cyclohexanols. Depending on the experimental conditions, hydrogenation of phenol yields either pure cyclohexanol or a mixture of it with cyclohexanone, cyclohexane, and benzene. Sabatier[1] assumed that cyclohexanone is obtained as a result of the decomposition of cyclohexanol. Ipat'ev[9,10], however, regarded cyclohexanone as the primary product of hydrogenation, subsequent reduction of which yields cyclohexanol. On the basis of these views he suggested the following scheme for the hydrogenation:



He regarded this scheme as confirmed by the fact that at higher temperatures no ketone was obtained, although its formation would be expected from the Sabatier scheme. The same scheme was put forward by Skita and Ritter[59], who, on hydrogenating phenol by the Sabatier method at 100°–120° on nickel, found that hydrogenation of the phenol is accompanied by a partial dehydration of cyclohexanol to cyclohexene with hydrogenation of the latter to cyclohexane, part of which is dehydrogenated to benzene. The formation of cyclohexanone as an intermediate product in the hydrogenation of phenol to cyclohexanol was demonstrated also by the work of Vavon[60-62] and Grignard[63-65]. Ando[66] showed that when reaction is carried out in the absence of hydrogen and at temperatures above 250° the reverse reaction, the formation of the ketone from cyclohexanol, can occur. Under the conditions of the hydrogenation of phenol to cyclohexanol, there is a partial dehydration of cyclohexanol with the formation of cyclohexene and water, the former being hydrogenated to cyclohexane.

The results obtained by Ipat'ev and other investigators on the mechanism of the hydrogenation of phenols were later confirmed by kinetic measurements. The kinetics of the catalytic hydrogenation of phenol in the liquid phase were studied by Jungers and his collaborators[67], who showed that hydrogenation does in fact proceed via the formation of cyclohexanone. The rate of hydrogenation of cyclohexanone to the alcohol was found to be greater than its rate of formation from phenol. The activation energies for the formation of cyclohexanone and for its reduction to cyclohexanol proved to be 8500 and 6500 cal/mole respectively. The order of reaction for the hydrogenation of phenols to hydroaromatic alcohols evidently lies between one and zero[68,69].

The vapour-phase hydrogenation of phenols at normal pressures occurs in the same way as the liquid-phase hydrogenation at high pressures, i.e. via the intermediate formation of the ketone[42].

Published data on the configuration of the geometric isomers of the hydroaromatic alcohols are very contradictory. The production of one or other geometric isomer of the alcohol depends on the conditions of hydrogenation. Patents obtained by Schering–Kahlbaum[70,71] describe the hydrogenation of an aqueous solution of sodium *p*-cresate on

nickel under pressure to form *trans*-4-methylcyclohexanol. Braun and Haensel[72] hydrogenated the symmetrical xylenol in the presence of a nickel catalyst in an autoclave at 230° and obtained a mixture of the *cis*- and *trans*-isomers of the corresponding alcohol and ketone; the content of both *trans*-isomers was increased with decrease in the amount of hydrogen absorbed by the xylenol. Skita[73] found the formation of the *trans*- or *cis*-form of the alcohol to be strongly dependent on the temperature of hydrogenation and the pH of the medium. On hydrogenating *o*-, *m*-, and *p*-cresols in the presence of colloidal platinum in a strongly acid medium (a mixture of acetic and hydrochloric acids) at 2–3 atm and 70°, he obtained all three methylcyclohexanols in the *cis*-form. On hydrogenation in neutral or alkaline medium at room temperature, the *trans*-isomers were obtained; a weakly acid medium yielded a mixture of *cis*- and *trans*-isomers. Similar results were obtained by Vavon[61,62] who hydrogenated *o*-propylphenol and *o*- and *p*-isopropylphenols in the presence of platinum black.

The hydrogenation of *o*- and *p*-cresols in the presence of a nickel catalyst at 150° and high pressures yielded predominantly *trans*-2- and *trans*-4-methylcyclohexanols[22,74,75], as did hydrogenation in the presence of a copper–chromium catalyst[76]. Hydrogenation of *o*- and *p*-cresols at room temperature, both in the presence of platinum oxide by the Adams method[77] and in the presence of Raney nickel[78] in methyl alcohol, yielded the corresponding methylcyclohexanols with the *cis*-forms predominating.

Preferential formation of the *cis*-isomer was also observed in the hydrogenation of *p*-t-butylphenol in the presence of a rhodium catalyst[79].

For a long time mistaken views were held as to the properties of the *cis*- and *trans*-isomers of 3-methylcyclohexanol. It has now been proved[80–82] that the isomer of 3-methylcyclohexanol which Skita[73,83] regarded as the *trans*-isomer, and which was accepted as such in several other papers[21,84], is in actual fact the *cis*-isomer. It has been shown that, in conformity with the concept of axial and equatorial bonds, the *cis*-configuration of 3-methylcyclohexanol is the most stable. This isomer has a lower density and a lower refractive index, in opposition to the Auwers–Skita rule. New data have also been obtained on the stereoisomerism of the 2,5-dimethylcyclohexanols[85].

From a study of the hydrogenation of the cresols and the corresponding alicyclic ketones, Peppiatt and Wicker[86] concluded that hydrogenation at room temperature always leads to the formation of alcohols with a high content of the isomer containing an axial (polar) hydroxyl group, i.e. the *cis*-1,2-, *trans*-1,3-, and *cis*-1,4-isomers; raising the temperature (100°–200°) enriches the mixture in the other isomer. These authors explain the contradictory results in the literature by the possible isomerisation of the isomers obtained initially under the conditions of hydrogenation, since at elevated temperatures nickel and platinum catalysts containing a minute amount of alkali catalyse the interconversion of the *cis*- and *trans*-forms[78,86].

Table 1 gives the properties of *cis*- and *trans*-methylcyclohexanols and the melting points of their derivatives based on results obtained by different workers. The considerable differences in the melting points of several of these derivatives are evidently to be explained by incomplete separation of their isomers, and possibly also by polymorphism, which is particularly characteristic of derivatives of 3-methylcyclohexanol. At the present time, thanks to progress in the stereochemistry of the cycloalkanes[87–89], methods have been worked out for the preferential production of the *cis*- or the *trans*-isomers of alkylcyclohexanols, and more reliable values have been obtained for the properties of their derivatives[22,75,90]. Heats of combustion of the methylcyclohexanols are given in the paper by Eliel and Haber[91].

TABLE 1. Properties of methycyclohexanols and their derivatives.

Methylcyclohexanol	B.P., °C/mm Hg	d_4^{20}	$d_4^{t°}$	n_D^{20}	Melting points of derivatives, °C								reference
					o-nitrobenzoate	*p*-nitrobenzoate	3,5-dinitrobenzoate	acid phthalate	α-naphthylurethane	phenylurethane	*p*-aminobenzoate	acid succinate	*p*-toluenesulphonate	
cis-2-	77–78/20	—	0.9228(25)	—	—	35–36	—	89–90	—	78–80	—	30–31	—	84
	—	0.9337	—	1.4640	—	—	98–99	—	—	90–91	—	—	—	83
	50.5/2.9	—	0.9274(30)	1.4649	oil	56–57	100–101	102–104	112	92–93	—	—	—	22
	60.4/12	0.9360	0.9118(25)	1.4653	—	54.8–55.6	—	103.8–105.0	—	92,6–93,4	—	—	56,7–57.2	75
trans-2-	79/20	—	0.9228(25)	—	—	65	—	124–125	—	105–106	—	44–46	27–28	84
	—	0.9238	—	1.4611	—	—	114–115	—	—	105–106	—	—	—	83
	53.0/3,5	—	0.9174(30)	1.4616	60–60.5	64.5–65	117	124–125	156	105	—	—	—	22
	66.7/12	0.9247	0.9208(25)	1.4616	—	63.7–64.2	—	125,2–125.8	—	105.2–105.5	—	—	27.5–28.4	75
cis-4-	78–79/20	—	0.9180(25)	—	—	94	—	72–73	—	124	—	—	—	84
	—	0.914	—	1.4549	—	—	133–134	—	—	118–119	—	—	—	83
	52.0/2.0	—	0.9173(30)	1.4614	oil	—	106–107	84–85	106–107	103–104	—	—	—	22
trans-4-	78–79/20	—	0.9080(25)	—	—	67	—	119–120	—	124–125	—	—	71–72	84
	—	0.913	—	1.4534	—	—	139–140	—	—	124–125	—	—	—	83
	54.0/3.0	—	0.9040(30)	1.4561	68	64–65	142	120–121	159,5–160	124–124.5	—	—	—	22
cis-3*	78–79/20	—	0.9104(25)	—	—	58	—	93–94	—	92–94	—	oil	39–40	84
	—	—	0.9072(30)	1.4573	—	48	99	—	130	92	—	—	—	21
	—	0.9155	0.9065(30)	1.4572	—	45.5–46.5	—	—	—	—	141.5–142.5	28.4–29	34–34.4	90
trans-3*	77–78/20	—	0.9091(25)	—	—	65	—	82–83	—	101–103	—	—	46–47	84
	—	—	0.9137(30)	1.4583	—	63	111	—	118	93–91;α–103;	—	—	—	21
	—	0.9214	0.9138(30)	1.4590	—	83–83.5	—	68–71	—	91	111–112	48.5–49.0	18.6–19.2	90

* In refs. 21 and 84, the *cis*-isomer is denoted as *trans*, and the *trans*-form is regarded as the *cis*-isomer.

II. HYDROGENATION OF PHENOLS TO HYDROAROMATIC KETONES

As has been indicated above, cyclohexanone is an intermediate product in the hydrogenation of phenol to cyclohexanol. Hydrogenation of the ketone takes place more rapidly than its formation from phenol, which makes it difficult to carry out the hydrogenation in such a way that the process can be stopped at the stage of formation of the ketone. The position is still further complicated by the fact that cyclohexanone and similar ketones, even on hydrogenation under mild conditions, yield an appreciable quantity of phenols [92,93], as a result of a dismutation (disproportionation) reaction:

$$3C_6H_{10}O \rightleftharpoons C_6H_5OH + 2C_6H_{11}OH.$$

Nazarov et al. [94] observed that cyclohexanone underwent this reaction in the presence of aluminium oxide at 390°–450°.

According to Zil'berman [95], the dismutation of cyclohexanone is thermodynamically possible over the temperature range 289°–700°K, and may be operative during the catalytic synthesis of this compound. He obtained 35% of the ketone on passing the vapours of phenol and cyclohexanol (at a molar ratio of 1 : 2) over a nickel-containing catalyst heated to 150°–200°.

A review of the literature on the hydrogenation of phenols to hydroaromatic alcohols shows that many investigators have obtained alcohols mixed with the ketone, but in the majority of cases the amount of the latter did not exceed 10–15%. Ando [66], on hydrogenating phenol in the presence of reduced nickel at 260° and 48 atm, obtained 37% of cyclohexanone. Skita [73] obtained 80% of methylcyclohexanone by the controlled absorption of hydrogen by *o*-cresol in the presence of colloidal platinum in a neutral medium at 70°. Barney and Hass [96], by the catalytic hydrogenation of thymol in aqueous alkali at 150°–160° and 42 atm, obtained the corresponding ketone in 80% yield (based on the phenol consumed). In 1958 Joris and Vitrone [97] patented the selective hydrogenation of phenol to cyclohexanone in the presence of palladised charcoal. The hydrogenation products contained 79% of cyclohexanone.

In view of the unavoidability of obtaining a mixture of alcohol and ketone, several workers have recommended that the hydrogenation of phenols should be carried out in two stages: (1) complete hydrogenation in some way to yield a mixture of alcohol and ketone, and (2) dehydrogenation of alcohol to ketone [29,99]. Chinese investigators have prepared cyclohexanone in this way [98]. Cyclohexanol was obtained by hydrogenation of phenol on a nickel–kaolin catalyst at 140° and 80 atm, and then dehydrogenated to the ketone (yield 55%) in a flow system at 250°–300° under reduced pressure (155 mm) in the presence of copper on asbestos. Barney and Hass [96] carried out a direct quantitative dehydrogenation of menthol (crude hydrogenated thymol) by fractionation on an efficient column in a flask filled with Adkins' copper–chromium catalyst.

A partial hydrogenation of phenols cannot always be achieved even in the case of sterically hindered polyalkylphenols. Whitaker [100] showed that the structure of the polyalkylphenol determines the products which can be obtained by its hydrogenation. If one *ortho*-position in the phenol is unoccupied, its partial hydrogenation to the ketone may be impossible, even if the other *ortho*-position is occupied by a strongly shielding group, such as t-butyl. With a methyl and a t-butyl group in the *ortho*-positions, either the alcohol or the ketone may be obtained, depending on the conditions. If, however, both *ortho*-positions are occupied by strongly shielding groups, ketones alone are obtained, and hydrogenation to the alcohol does not occur. These results are in agreement with the data of Whitmore [101] on the effect of steric hindrance on the behaviour of ketones under hydrogenation conditions.

Whitaker [100], by the hydrogenation of polyalkylphenols in the presence of Raney nickel (10%) at 140°–240° and 85–175 atm, obtained the following alcohols and ketones which had not been described previously: 6-t-butyl-3-methyl-, 4,6-di-t-butyl-2-methyl-, 4,6-di-t-butyl-3-methyl-, and 6-t-butyl-2-methylcyclohexanols; 6-t-butyl-2-methyl-, 4,6-di-t-butyl-2-methyl-, 2,4,6-tri-t-butyl-, and 2,6-di-t--butyl-4-methylcyclohexanones; and 2,6-di-t-butyl-4--methylcyclohex-2-enone.

Thus, it is possible in principle to obtain alicyclic ketones by the hydrogenation of the corresponding phenols, but the yield of ketone depends not only on the conditions of hydrogenation, the nature of the catalyst, and the amount of hydrogen absorbed, but also on the structure of the original phenol.

III. REDUCTION OF PHENOLS TO AROMATIC HYDROCARBONS

The reduction of phenols to aromatic hydrocarbons was of interest long ago from the point of view of exploiting the phenols in primary tars. This mode of hydrogenation of phenols has been the most fully studied, and is widely represented in the literature.

Smith [102] in 1890 was the first to direct attention to the formation of benzene and toluene by passing phenol and cresol through a heated tube filled with carbon. However, the yield of hydrocarbons was low [103–105]. Kling and Florentin [106] obtained 35% of hydrocarbons by heating technical cresol at 480° and 80 atm in the presence of aluminium chloride. Ipat'ev and Orlov [107] were able to effect partial conversion of phenol into benzene and of cresol into a mixture of benzene and toluene in the presence of alumina and copper oxide. There are numerous papers on the reduction of phenols to aromatic hydrocarbons published by the school of F. Fischer [108], who showed that the lower phenols (cresols, xylenols, and technical phenolic mixtures) can be reduced by hydrogen to aromatic hydrocarbons by passing them through an iron tube, coated with zinc or sulphur, at 700°–750°. Reduction of phenol homologues is accompanied by a partial elimination of methyl groups. For example, cresol yielded a 5 : 1 mixture of benzene and toluene with a total yield of 65–78%. The formation of aromatic hydrocarbons from phenols, especially cresols, also takes place at such high temperatures in the absence of a catalyst, but the yield is then comparatively low [109].

The work of Fischer gave an impetus to many investigations on these lines. The efforts of research workers were directed towards lowering the reaction temperature and selecting active catalysts which were resistant to poisoning. It was suggested that dehydrating oxide catalysts such as the oxides of aluminium, thorium, and chromium [110–112], which are stable to the action of catalyst poisons, should be used for the reduction of phenols to aromatic hydrocarbons. It was found, however, that dehydrating catalysts are most effective when activated by small amounts of hydrogenation catalysts [113,114] or when these oxides are used as carriers for the latter [115–117].

Hydrogenation catalysts based on metal oxides and sulphides proved to be effective for the reduction of phenols to hydrocarbons. These catalysts were introduced as the result of the work of the IG. Farbenindustrie AG. on the Bergius process for obtaining petrol from coal. They possess several advantages compared with metallic catalysts, for they are resistant to poisoning and are effective at high temperatures. Catalysts based on molybdenum have been most widely used. Molybdenum oxide was found to be effective for the hydrogenation not only of individual phenols but also of their technical mixtures, in particular for the reduction of "tricresol"[118], and also the phenolic oil from low-temperature tar[119-121]. Active molybdenum oxide can be prepared in various ways — from ammonium molybdate, from molybdic acid, or by dissolving the metal in nitric acid and then heating[122] — but technical molybdenum oxide is inactive. Bahr and Petrick[123] noted that the activity of molybdenum oxide diminishes under the conditions of hydrogenation of phenolic tars at atmospheric pressure, and suggested this was the result of the conversion of the active molybdenum trioxide into the less active dioxide. However, a special study of the origin of the molybdenum oxide and X-ray analysis of its structure did not support this hypothesis. It was found that the active hydrogenation catalyst was actually the dioxide, produced by reduction of the molybdenum trioxide in the course of the reaction[124,125]. The essential factor in producing an active catalyst is evidently not the mode of preparation of the molybdenum oxide but its subsequent reduction to the lower oxide. Maslyanskii and Shenderovich[124], studying the preparation of catalysts for the destructive hydrogenation of fuel, found that the greatest catalytic activity is obtained on complete reduction of MoO_3 to MoO_2. The optimum temperature for reduction was determined as about 300° for hydrogen pressures of both 50 and 200 atm. Either raising or lowering the temperature of reduction appreciably diminished the activity of the catalyst. When molybdenum oxide was used on a carrier, its activity varied to a considerably smaller extent with change in the conditions of reduction.

The reduction of phenols in the presence of molybdenum oxide can be carried out at either high or ordinary pressures, a temperature of about 325°–450° being adequate in the latter case. Newall[109] obtained 70% of toluene, 10% of other liquid hydrocarbons, and 14% of water by the hydrogenation of a cresol fraction of a tar from cracking, using atmospheric pressure, 450°, and a volume flow rate of $0.2\ h^{-1}$ and in the presence of molybdenum oxide deposited on activated wood charcoal. However, the rate of hydrogenation of phenols is directly related to the hydrogen concentration. Increase in the pressure of hydrogen greatly shortens the time required for the process and to some extent lessens the formation of coke. It is therefore more economical to carry out the process at high pressure, but this, as will be shown below, limits the yield of the required hydrocarbons.

The activity of molybdenum catalysts is raised by the addition of copper, chromium oxide[122,123,126], and especially sulphur or its compounds. The promoting action of sulphur and its compounds in the reduction of phenols was noted in several papers[127-131]. Tropsch[118] investigated the catalytic effect of a series of sulphur compounds on the hydrogenation of a technical mixture of cresols and found the sulphides of molybdenum, tungsten, and cobalt to be the most active. Moldavskii and Prokopchuk[132] and Prokopets and Eru[133] showed that the most convenient is an MoS_2 catalyst obtained by reduction of MoS_3, since the latter, like MoO_3, is not very stable and gives irreproducible results, being converted during the process into MoS_2.

Moldavskii and Lifshits[5] investigated in detail the influence of physical factors on the hydrogenation of phenol and *o*-cresol in the presence of 5% of MoS_2 in an autoclave. They showed that at 350°–370° and 25–50 atm, phenol and *o*-cresol are readily reduced to a mixture of aromatic hydrocarbons and naphthenes. The results were checked with technical phenolic mixtures (oils from the primary tar of Cheremkhovo coals) containing 50% of phenols[134]. Experiments carried out both in an autoclave and using a continuous plant gave good results in the presence of molybdenum disulphide deposited on clay (1 : 9). Tricresol at 400° and 15–40 atm yielded 72.5% of toluene, 1.5% of unsaturated compounds, and 5–10% of methylcyclohexane; the higher phenols yielded a petrol of the same quality as obtained from individual phenols. Moldavskii and Lifshits showed that hydrogen acts on phenols in two independent ways:

1. Reduction of the phenol with formation of an aromatic hydrocarbon and water:

$$C_6H_5OH \xrightarrow{H_2} C_6H_6 + H_2O.$$

2. Hydrogenation of the ring, via a series of intermediate stages, the result being a hydroaromatic hydrocarbon:

$$C_6H_5OH \xrightarrow{3H_2} C_6H_{11}OH \xrightarrow[-H_2O]{} C_6H_{10} \xrightarrow{H_2} C_6H_{12}.$$

The formation of cyclohexane by the hydrogenation of benzene occurs to a very slight extent, if at all. Special experiments have shown that in the presence of MoS_2 at 350° and 100 atm not more than 3–4% of the benzene and toluene has undergone hydrogenation. In the presence of molybdenum oxide at 400°–450° and 65–100 atm, benzene is not hydrogenated, whereas phenol is converted into cyclohexane to the extent of 10–30%[135]. Further, phenol, as Klimov and Bogdanov[136] have shown, exerts an inhibiting effect on the hydrogenation of aromatic hydrocarbons. The formation of benzene from cyclohexane at high pressures and in the presence of a hydrogenating catalyst is also unlikely. Thus the formation of benzene by the hydrogenation of phenol in the presence of molybdenum catalysts at high temperatures and pressures is a result of the direct reduction of the phenol. The bulk of the cyclohexane is formed by the dehydration of cyclohexanol with subsequent hydrogenation of the cyclohexene formed. This picture of the mechanism of formation of aromatic and hydroaromatic hydrocarbons under these conditions agrees with the views of Roberti[137], Cawley[138], and Ando[139]. Cyclohexene (or methylcyclohexene) has been detected among the reaction products, but it has not yet been possible to detect the alcohols. A series of papers have described the behaviour of cyclohexanol at 340°–470° and 100 atm in the presence of ammonium molybdate[128], wood charcoal impregnated with molybdic acid[138], molybdenum oxide and sulphide[140], and also cobalt sulphide[137]; it was shown that cyclohexanol is completely converted into cyclohexane. Moldavskii and Lifshits[5] found that lowering the hydrogen pressure favours the first reaction, but raising the pressure increases the content of hydroaromatic hydrocarbons. Thus when the pressure of hydrogen was raised from 50 to 150 atm the quantity of aromatic compounds in the petrol fell from 84.7 to 66.4%. Ando[141], by the hydrogenation of the phenolic fraction of low-temperature tar using MoO_3 at 465° and 250 atm, obtained 77% of hydrocarbons consisting of about equal proportions of aromatic

compounds and naphthenes. When the pressure was diminished to 50–100 atm, a hydrocarbon mixture was obtained, containing, depending on the conditions, 14–74% of naphthenic and 23–86% of aromatic compounds[142]. Cawley[138] obtained 37% of C_6H_{12} and 25% of benzene from phenol in the presence of wood charcoal impregnated with ammonium molybdate, at 100 atm and 400°, and, at 450°, 35% of cyclohexane and 44% of benzene. Moldavskii and Lifshits[5] calculated the mean rates of reduction and hydrogenation of phenol and *o*-cresol from experimental results. They found that at pressures above 20 atm the rate of hydrogenation is directly proportional to the pressure of hydrogen. Measurement of the temperature coefficient of the reaction showed that within the range 330°–370° the rate of reaction of phenol over MoS_2 increases considerably with rise in temperature. The temperature coefficients for these reactions with phenol and *o*-cresol were found to be 1.42–1.60. The activation energies amounted to 37 000 for the reduction and for the hydrogenation of phenol, 27 000 for the reduction of *o*-cresol, and 33 000 cal/mole for the hydrogenation of the latter. Bobyshev et al.[143] have determined the temperature coefficient of the hydrogenation of phenol, in the presence of MoS_2 at 200 atm over the range 350°–400°, as 1.36–1.40, and the energy of activation as 24 000–28 000 cal/mole.

Thus experimental and thermodynamic data show that in the hydrogenation of phenols in the presence of molybdenum catalysts a decrease in pressure produces an increase in the amount of aromatic hydrocarbons, but this is accompanied by a retardation of the reaction and an increase in coke formation. At high temperatures phenols tend to undergo various condensation and polymerisation reactions. Among the products which have been detected are diphenyl ether and bicyclohexyl[144], *p*-cyclohexylphenol and cyclohexylbenzene[5], and bicyclohexyl and its isomers[145]. All these products may serve as material for coke formation. In view of this, Rapoport et al.[146] proposed that the conversion of phenols into aromatic hydrocarbons should be carried out in two stages, by (1) obtaining a mixture of aromatic and hydroaromatic hydrocarbons at 370°–430° and 90 atm hydrogen pressure, and (2) dehydrogenating this mixture in the vapour phase at 450°–500° and a lower pressure (20–40 atm) to aromatic hydrocarbons. A 1952 German patent[114] also recommends a stepwise production of aromatic hydrocarbons from high-boiling phenols or oils which are rich in phenols.

In order to obtain from phenols hydrocarbons which are rich in aromatic compounds and contain only a small amount of naphthenes, Bahr[126,147] recommended carrying out the reduction of phenols not with hydrogen itself but with a diluted form of the gas, e.g. water gas. When pure hydrogen was used, he replaced the molybdenum catalyst by a less active iron–copper (1 : 1) catalyst. When phenol was hydrogenated in the presence of such a catalyst at 400°–450° and 30 atm, the content of hydroaromatic hydrocarbons did not exceed 5–9%. Japanese investigators[148] recommend the employment of an iron oxide catalyst on a carrier with added nickel and chromium, and that the hydrogenation of phenols should be carried out at atmospheric pressure.

When phenol is hydrogenated in the presence of an iron oxide catalyst at pressures of the order of 150 atm, the main product is cyclohexane[136]. A high content of aromatic hydrocarbons among the products of the hydrogenation of phenols is characteristic of tungsten sulphide even at high pressures of hydrogen[136,149]. The hydrocarbon portion of the product of the hydrogenation of phenol at 400°–420° and 150 atm in this case consisted of 75–85% of benzene[136]. The hydrogenation of phenols in the presence of either iron or tungsten catalysts, which form the basis of industrial catalysts for the destructive hydrogenation of various forms of fuel, has been insufficiently discussed in the literature. Data exist pointing to the suitability of using a tungsten catalyst together with nickel[111,150], the presence of which diminishes the cracking and isomerising effect of tungsten sulphide[151].

The dependence of the rate of reduction of phenols on their structure has been inadequately studied up to the present. Bobyshev et al.[143] measured the relative rates of reduction of eleven monohydric phenols and thiophenols to aromatic hydrocarbons at 350° and an operating hydrogen pressure of ~ 100 atm in the presence of MoS_2 when the reaction was not more than 30% complete. They observed no great differences in the rates of reduction of phenols with variation in the size, number, and position of alkyl substituents. The majority of phenol homologues are reduced at about 70% of the rate for phenol itself, naphthols are reduced twice as rapidly, and thiophenol 28 times as rapidly, as phenol.

The reduction of alkylphenols to aromatic hydrocarbons can be employed also as a preparative and analytical method to obtain individual aromatic hydrocarbons. For this purpose the corresponding aryl diethyl phosphates or toluene-*p*-sulphonates are first prepared, and they are then reduced to the corresponding hydrocarbons[152–154].

At the present time the reduction of phenols to aromatic hydrocarbons is of no great practical interest, since the phenols themselves and their hydrogenation products — hydroaromatic alcohols — form a valuable raw material for the chemical industry, enjoying a wide application in different branches of the national economy.

IV. PRODUCTION OF HYDROAROMATIC HYDROCARBONS

Hydroaromatic hydrocarbons are obtained in the course of the hydrogenation of phenols mainly as a result of dehydration of hydroaromatic alcohols, as was indicated above. The formation of hydroaromatic hydrocarbons during the hydrogenation of phenols to the corresponding alcohols has been observed by many investigators, but only small amounts were obtained and they were accompanied by the main product of hydrogenation, the hydroaromatic alcohol. For the preferential production of the alicyclic hydrocarbon it is necessary to carry out hydrogenation at a higher temperature to ensure dehydration of the alcohol. Ando[66,155] showed that, whereas at 150°–250° and with high pressures in the presence of reduced nickel cyclohexanol is obtained from phenol, at 250°–350° it is completely dehydrated to cyclohexene, and then converted into cyclohexane, which does not change further on heating to 470°. Ando was able to obtain almost pure cyclohexane from phenol at 470° and an initial hydrogen pressure of 117 atm. Skita[31] obtained a 40% yield of 1,3-dimethylcyclohexane by the hydrogenation of 3,5-xylenol in the presence of colloidal platinum at 250° and 50 atm. Hydroaromatic hydrocarbons can be obtained from phenols at comparatively low temperatures and normal pressures in the presence of a nickel catalyst. Thus Shuikin et al.[27] obtained methylcyclohexane in 71% yield by hydrogenating *o*-cresol in a flow system at 175°, employing as catalyst nickel (20%) deposited on aluminium oxide; 3,4-xylenol at 200° produced 1,2-dimethylcyclohexane with a yield of 62%[28].

When phenols are hydrogenated on oxide catalysts, a mixture of aromatic and hydroaromatic hydrocarbons is usually obtained, the proportion of the latter being greatest in the presence of nickel oxide[156] and less with hydrogenation on a molybdenum and especially a tungsten catalyst[118,141,149]. However, hydrogenolysis with the formation of lower aliphatic hydrocarbons occurs to a greater extent on a nickel catalyst[113].

Alekseeva and Moldavskii[157] obtained mainly naphthenic hydrocarbons in the vapour-phase hydrogenation of phenols in the presence of the industrial catalyst WS_2 + NiS + Al_2O_3. The quantity of aromatic hydrocarbons depended on the structure of the initial phenol. Alkylated phenols gave a greater quantity of aromatic compounds. Thus with phenol, *o*- and *p*-cresol, and n-butylphenol the contents of aromatic hydrocarbons were 4, 5.5, 7, and 15% respectively. The proportions of aromatic hydrocarbons and naphthenes varied also with the conditions of hydrogenation, higher pressures favouring the formation of hydroaromatic hydrocarbons. Cawley[158] gives the following extents of conversion of phenol into hydrocarbons at various temperatures, in the presence of molybdenum disulphide, with a hydrogen pressure of 200 atm and a period of contact of 5 sec: at 250° there is 9.4% conversion, the proportions of benzene and cyclohexane being 0.9 : 1; at 300° conversion reaches 62%, at 350° 98.5%, and at 400° 100%, the ratio $C_6H_6 : C_6H_{12}$ becoming equal to 0.08 : 1. Hydroaromatic hydrocarbons are obtained in high yield by the hydrogenation of phenols in the presence of cobalt sulphide. Roberti[137] obtained predominantly naphthenic hydrocarbons by hydrogenating the phenols in primary tar in the presence of cobalt sulphide at 300° and an operating hydrogen pressure of 100 atm. With the same catalyst at 370° and 50–90 atm, Tropsch[118] obtained methylcyclohexane from a technical mixture of cresols.

Hydroaromatic hydrocarbons obtained from phenols usually contain some cyclopentane hydrocarbons, especially when the isomerising catalysts MoS_2 and WS_2 have been used. When phenol is hydrogenated, more methylcyclopentane is obtained than is usually formed by the isomerisation of cyclohexene under similar conditions[140,159,160].

V. HYDROGENATION OF POLYHYDRIC PHENOLS

Polyhydric phenols are contained in the tars obtained by fractionating and processing various mineral fuels. Their behaviour on hydrogenation has been inadequately studied. Polyhydric phenols are thermally less stable than monohydric phenols, and show an increased tendency to undergo decomposition, condensation, and other reactions[107,128,136,141,158]. Cyclohexanediols can be obtained by the hydrogenation of dihydric phenols in the presence of a nickel catalyst in ethyl alcohol at 130°–140° and 70–80 atm; hydrogenation of 800 g of resorcinol under these conditions yielded 250 g of a mixture of diols and 150 g of cyclohexanol; 800 g of quinol yielded 650 g of diols (84% of the *cis*- and 16% of the *trans*-isomer of cyclohexane-1,4-diol) and 32 g of cyclohexanol[161]. Pure cyclohexane-*trans*-1,4-diol is best prepared by hydrolysis of its diacetate, which can be separated from the products of the acetylation of the mixture of the *cis*- and *trans*-1,4-diols obtained by the hydrogenation of quinol[162].

Fujita[163] obtained cyclohexanediols and cyclohexanetriols by the hydrogenation of the corresponding dihydric and trihydric phenols at 180° and 100 atm in the presence of a nickel catalyst prepared by precipitating a 10% solution of nickel nitrate with 10% alkali and reducing the product at 320°. Hydrogenation of resorcinol yielded 48% of cyclohexane-1,3-diol, 19% of cyclohexanol, and 7% of the monocyclohexyl ether of resorcinol. Catechol under the same conditions gave cyclohexane-1,2-diol in 71% yield; hydrogenation of quinol resulted in a 94% yield of cyclohexane-1,4-diol. The rate of hydrogenation of dihydric phenols in the presence of Raney nickel at 175° and 100 atm is increased by the addition of a small quantity of water; under these conditions the side-reactions which normally diminish the yield of diols are markedly suppressed[164]. According to the patent literature, cyclohexanediols can be obtained also by the hydrogenation of the corresponding phenols in the presence of ruthenium and rhodium catalysts[165,166]. The hydrogenation of polyalkylphenols in the presence of "modified" Raney nickel has been discussed by Anderson[167,168].

This brief summary shows that polyhydric alicyclic alcohols can be obtained by the hydrogenation of the corresponding polyhydric phenols under considerably milder conditions than those required for the hydrogenation of monohydric phenols.

Hydrogenation of polyhydric phenols at high pressures in the presence of molybdenum catalysts results in the formation of hydrocarbon mixtures containing aromatic, hydroaromatic, and various other hydrocarbons; formation of phenol is also observed.

VI. DESTRUCTIVE HYDROGENATION OF HIGHER PHENOLS WITH THE FORMATION OF LOWER PHENOLS

Many investigators have noted an increase in the proportion of lower phenols in the course of the destructive hydrogenation of tars and coals. Thus Tropsch and Ter-Nedden[6], in the hydrogenation of a brown-coal semi-coke at 460° and 200–260 atm, obtained 22% of phenols, two-thirds of which consisted of phenol itself, and the cresols. Rapoport et al.[169], by the destructive hydrogenation of Chelyabinsk tar in a continuous plant at 430° and 150 atm, in the presence of molybdenum trioxide, found that the petrol fraction with b.p. up to 200° contained ~40% of phenols (phenol, cresols, and xylenols). Storch and his collaborators[170] found that the product of the hydrogenation of a coal slurry contained 25% of phenols; when this was hydrogenated further, an additional 25% of lower phenols was obtained. Koshel'[171] observed that, when certain fractions of the primary tar from Ukrainian brown coals were hydrogenated in the presence of nickel sulphide at 100–200 atm in a flow system, the content of lower phenols rose from 9% in the initial raw material to 12% in the product. Lanin et al.[172] found that liquid-phase hydrogenation of Cheremkhovo coal-tar in the presence of an iron catalyst at 460° and 300 atm yielded a product containing 32.2% of phenols, 57% of which were lower phenols. Similar observations have been recorded in several other papers[173–177].

The dealkylation of phenols is thermodynamically possible. Calculations of the equilibrium constants for the demethylation of the cresols show that phenol itself can thus be obtained in good yield[178,179].

Phenols may be dealkylated during the cracking of higher phenols even in the absence of catalysts at high temperatures, but with a low yield of lower phenols[180–184]. In addition, considerable coke formation makes the process impracticable. Dealkylation of phenols under conditions of catalytic hydrogenation considerably diminishes coke formation Such catalysts as the oxides of iron, aluminium, and

tungsten, as well as the sulphides of iron, nickel, cadmium, zinc, tungsten, and other metals, favour the splitting off of alkyl groups from phenols. In practice, however, the process is complicated at high temperatures by condensation and dehydroxylation reactions. Zabavin[185], by passing phenolic fractions together with hydrogen through an iron tube treated with hydrogen sulphide and filled with lumps of ferrous sulphide at 650°–660°, obtained, together with the phenol–cresol fraction, a considerable quantity of hydrocarbons of the benzene series and a compound containing fused benzene nuclei. A great percentage of neutral oil, to the detriment of the yield of lower phenols, was also obtained by Hagemann and Neuhaus[178] in the high-temperature treatment of phenols with hydrogen in the presence of Fe_2O_3. They recommend that condensation and polymerisation reactions should be avoided by carrying out the hydrogenation in an inert solvent, e.g. benzene. However, even in the presence of benzene they were unable to achieve a high yield of lower phenols. Carrying out the reaction in caustic soda solution and in the presence of molybdenum catalysts did not give good results, owing to considerable dehydroxylation[186]. However, according to certain patent claims, the use of alkali is advantageous[187].

Kuznetsov and Belov[188,189] and also Konov[190] have shown that an increased yield of phenol from higher phenols, at the expense of the yield of aromatic hydrocarbons, is favoured by carrying out the reaction in the presence of water vapour.

Rapoport and Masina[191] investigated the hydrogenation of *o*-cresol at 510° in the presence of an iron catalyst, water vapour, and various solvents; using a pressure of 180 atm of steam and 5% Fe_2O_3, they obtained up to 25% of phenol. Benzene as solvent did not give positive results; in the presence of pyridine the yield of phenol was increased. Increasing the pressure of hydrogen and using hydrogenating catalyst additions, e.g. 1% MoS_3, contributed in a marked degree to the suppression of condensation reactions.

Kalechits and Salimgareeva[192] investigated the possibility of dealkylating the phenols of Cheremkhovo tar in the presence of an iron catalyst. They obtained the best yields of lower phenols by hydrogenating the tar at 480°–490° and 300–340 atm. A tar containing initially 12% of lower phenols yielded a product containing 55–75% of phenols boiling below 220° and consisting of phenol itself (21%), cresols (39.8%), and xylenols (19.4%)[193]. It was noted that substituents in the *para*-position to the hydroxyl were most readily eliminated, the *meta*-isomers being the most stable. The great stability of *meta*-isomers has been noted also in the thermal cracking of alkylphenols[194,195].

Research on the hydrogenation of Cheremkhovo tar, both in an autoclave and in a continuous plant carried out in the Institute of Mineral Fuel of the Academy of Sciences of the USSR, has shown[196] that lower phenols boiling below 230° can be conveniently obtained from phenols boiling at 230°–255°. These amount to 30–35% of all the higher phenols in the distillates of Cheremkhovo tar and its liquid-phase hydrogenation product boiling below 320°. The following conditions were used: complete reprocessing, 50–100 atm, 475°, a volume flow rate of 1 litre/h in the presence of Fe_2O_3 (1%) + Al_2O_3, and a 1 : 1 ratio between fresh higher phenols and those returned from the previous cycle. The yield of phenol, and cresols and xylenols was 57.4 and 39.4%, based on the phenols in the tar and in the product of its liquid-phase hydrogenation. The authors recommend a cyclic process of retreating the higher phenols and regeneration of the catalyst by burning out the coke with atmospheric oxygen. The behaviour of all the oxygen-containing compounds of Cheremkhovo tar on hydrogenation in the presence of iron oxide on coal at 420°–460° and 100–290 atm has also been studied by Alekseeva and Moldavskii[197].

For the production of lower phenols boiling below 225° by the destructive hydrogenation of the higher phenols in brown-coal tar, Perna and Pelčik[198] recommend a catalyst consisting of a mixture of tungsten and vanadium sulphides, which proved to be the most effective of all the catalysts which they examined (Al_2O_3, MoO_3, and their mixtures with Fe_2O_3 or Cr_2O_3). In the presence of 0.15–0.75% of this catalyst in aqueous ammonia at 460°–480° and an initial pressure of 30 atm, 55–57% of lower phenols were obtained, of which 19.5–21.5% represents phenol and cresols. Aqueous ammonia can be replaced by water (amount 20%) or pyridine. Under these conditions no polymerisation or condensation was observed, and reduction of the phenols to aromatic hydrocarbons was to a large extent inhibited.

Phenols may be dealkylated also in the absence of hydrogen, but polymerisation then occurs to a considerably greater extent, and a large amount of coke is formed. The hydrogen or other gas containing hydrogen in the dealkylation evidently saturates molecular fragments and unsaturated compounds, and in this way minimises coke formation. When the process is carried out by a flow method with a selective catalyst, the hydrogen can be dispensed with, the catalyst being regenerated periodically. This is particularly useful for the dealkylation of alkylphenols containing not less than four carbon atoms in the alkyl group, which readily lose the alkyl groups at comparatively low temperatures (350°–400°). In this case it is possible to obtain not only the simple phenols but also various unsaturated compounds.

Several recent patents have recommended that degradation of phenols should be carried out in the presence of oxides or sulphides of metals together with cracking catalysts[199–204]. Special researches by Vorozhtsov and Lisitsyn[205,206] and several other workers[207,208] have shown that on an aluminosilicate catalyst phenols undergo disproportionation, isomerisation, dealkylation, and reduction. By selecting appropriate conditions and additions to the catalyst, it is possible to achieve selectivity. Thus Luten and Good[209] patented the dealkylation of alkylphenols, containing not less than four carbon atoms in the alkyl group, by passing their vapours at a flow rate of 0.5–4.0 h^{-1}, 350°–400°, and normal pressure over a mixed synthetic catalyst of the $SiO_2 . Al_2O_3 . MgO$ type with added B_2O_3, ZnO_2, ThO_2, and V_2O_5; methyl and ethyl groups are not eliminated under these conditions. In the presence of water vapour, however, CH_3 groups also can be split off; thus *o*-cresol yielded 14.5% of phenol[210]. Butyl and more complex alkyl groups are readily eliminated as olefins on heating with phosphoric acid[211]. t-Butyl groups are easily split off at 225°–285° even in the absence of a catalyst[212,213].

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This brief review shows that the production of lower phenols from higher analogues has been insufficiently studied. Investigations have been unsystematic and disjointed. Little is known about the dealkylation of phenols in the course of their destructive hydrogenation. Only recently has research started on the changes undergone by

phenols in the presence of various aluminosilicate catalysts. The choice of conditions for the dealkylation of the higher phenols obviously depends on their structure. The dealkylation of alkylphenols containing four or more carbon atoms in the alkyl group can be accomplished comparatively readily at 300°–400° in the presence of various cracking catalysts, as well as in the presence of other oxide or sulphide catalysts. The elimination of alkyl groups containing one, two, or even three carbons atoms, however, requires more severe conditions. Increased demands are also made on the catalyst, especially in relation to its selectivity, since in this case greater importance attaches to competing reactions and in particular to the reduction of phenols to hydrocarbons. The dealkylation of such alkylphenols can be conveniently carried out at high pressures of hydrogen in the presence of nitrogenous bases or water vapour.

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THERMODYNAMICS AND THE STRUCTURE OF METALLIC ALLOYS

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INTRODUCTION

The atomic or molecular structure of solids is determined by the nature of the forces acting between particles. Crystal chemistry is based on the concept that solids acquire a crystal structure corresponding to the chemical bond

type. The thermodynamic method permits quantitative evaluation of the energy of interatomic bonds, but only if an equilibrium structure obtains and is known.

Practical problems often require predictions of the thermodynamic properties of condensed phases. A knowledge of the connection between the structure-sensitive properties of these phases and simple, known, and easily available data is also desirable. A complete solution of such a problem is obviously impossible unless due account is taken of all three of its facets: the crystal-chemical correspondence between bond type and crystal structure, theoretical analysis of the laws governing the interactions between particles, and verification that theoretical conclusions agree with the experimental results of thermodynamic studies.

In the past insufficient attention has been paid to the connection between the thermodynamic properties of metallic alloys and their structure and bond type. The experimental and theoretical study of the connection between alloy structure and thermodynamics has recently gained fresh impetus from work on heat-resisting alloys and semiconductor compounds, especially as regards the statistical theory of ordering processes and the experimental study of short-range ordering in alloys.

It seems desirable, therefore, to clarify the relationship between the structure and thermodynamics of metallic alloys from both the physicochemical and the physical viewpoints. The problem can be subdivided into a number of more or less independent but intimately interconnected sections.

First of all, the calculation of equilibrium thermodynamic properties of alloys on the basis of atomic properties in the light of solution theory must obviously rest on the statistical method. Attention must therefore be directed to statistical methods that are more or less convenient for calculating the thermodynamic functions of alloys. The most rational statistical methods require either the experimental determination or the theoretical calculation of the alloy (or solution) structure. In this connection the problem arises of establishing the link between the structure and the thermodynamic properties of alloys.

Crystal chemistry gave us a deeper insight into the nature of the chemical bond and the rules of formation of molecules and crystals. We can hope that the quantitative characterisation of the chemical bond by combined thermodynamical and structural data will enable us to systematise and generalise our knowledge of liquid and solid metallic alloys.

1. THERMODYNAMICS OF LIQUID ALLOYS WITH A EUTECTIC IN THE SOLID STATE

The formation of an alloy from the pure metals according to the reaction

$$a\,\mathrm{M} + b\,\mathrm{X} = \mathrm{M}_a\mathrm{X}_b \qquad (1)$$

is accompanied by a change in the free energy of the system

$$\Delta F = -RT\ln K_p, \qquad (2)$$

where K_p is the equilibrium constant, a change in the heat content

$$H_{\mathrm{M}_a\mathrm{X}_b} - (aH_{\mathrm{M}} + bH_{\mathrm{X}}) = \Delta H_T \qquad (3)$$

or

$$\Delta H_T = RT^2\frac{\partial \ln K_p}{\partial T}, \qquad (4)$$

and a change in the entropy

$$\Delta S_T = R\left(T\frac{\partial \ln K_p}{\partial T} - \ln K_p\right). \qquad (5)$$

The heat of formation can be experimentally determined by a direct calorimetric measurement of the heat evolved.

The entropy of formation of the alloy may be derived from heat-capacity data by means of the formula

$$\Delta S_T = \int_0^T \frac{\Delta C_p}{T}dT + S_0, \qquad (6)$$

where $S_0 = -R(N_1\ln N_1 + N_2\ln N_2)$ is the configurational entropy of mixing, which must be taken into account for the case of solid or liquid solutions, but not for compounds of stoichiometric composition.

In general, Eqn.(6) is inaccurate, since it is impossible in principle to separate the "configurational" from the "vibrational" entropy. Consequently both the entropy and the enthalpy of formation of the alloy are best determined indirectly from formulae (4) and (5), making use of the experimentally found value of K_p.

The concept of change in partial free energy is often invoked in the study of the thermodynamical properties of alloys:

$$\Delta\mu = \mu_p - \mu_0$$

where μ_p is the chemical potential of the given constituent in the alloy and μ_0 its chemical potential in the pure state; the change in partial enthalpy is

$$\Delta\overline{H} = T^2\frac{\partial(\Delta\mu/T)}{\partial T} \qquad (7)$$

and the change in partial entropy is

$$\Delta\overline{S} = -\frac{\partial\Delta\mu}{\partial T}. \qquad (8)$$

In experimental work it is usual to measure either the e.m.f. of the cell

$$\mathrm{M}_1\,|\,\mathrm{M}^+_{1(\mathrm{ion})}\,|\,(\mathrm{M}_1\mathrm{M}_{11})_{\text{alloy}}, \qquad (9)$$

which is related to $\Delta\mu$ by the expression

$$\Delta\mu = -23\,066\ zE, \qquad (10)$$

or the vapour pressure of one of the alloy constituents in the pure state (p_0) and in the solution (p_1), when

$$\Delta\mu = RT\ln p_1/p_0. \qquad (11)$$

The partial thermodynamic functions are then derived from formulae (7) and (8). The integral thermodynamic functions, referring to 1 mole of the alloy, are related to the partial quantities by the expression

$$\Delta G = N_1\Delta\overline{G}_1 + N_2\Delta\overline{G}_2. \qquad (12)$$

Alloy formation thus always results in a decrease in the free energy of the system and in the chemical potential of each of the constituents; enthalpy changes characterise the changes in interatomic-bond energy, and entropy changes describe the degree of randomness with which the atoms are distributed. Both functions are related to the atomic-interaction forces and the atomic structure of the alloy.

The present article is limited to consideration of the relation between short-range order and the thermodynamic properties of alloys. The restriction is justified, on the one hand, by the fact that interatomic forces are short--range forces, and, on the other, by the fact that short--range order is also determined by long-range order. The term "short-range order" usually refers to the number and kind of atomic neighbours surrounding a given atom, in the first, second, and possibly the third coordination shells.

In liquid metals and alloys short-range order is defined by the atomic radial distribution function $\rho(r)$, which gives the distribution of atoms in the space surrounding any given atom whose position is taken as the origin of the coordinate system. The number of atoms in a spherical shell $4\pi r^2 dr$, at a distance r from the central atom, is determined by the radial distribution function:

$$dn = \rho(r)\,4\pi r^2 dr.$$

Corresponding to this definition of the radial distribution function, the coordination number of a liquid is given by

$$z_1 = \int_{r_1}^{r_2} \rho(r)\,4\pi r^2 dr, \qquad (13)$$

where r_1 and r_2 are the radial distances from the given atom to the inner and the outer boundaries of the spherical coordination shell.

The radial distribution function is established experimentally from the diffraction of X-rays or electrons by the liquid[1].

From the results of experimental studies of the structure of liquid alloys, the presence of "microheterogeneity" and "stratification" can be expected, and, indeed, in some cases has been definitely established, within the domain of short-range order.

This phenomenon presents a simple picture: as far as nearest neighbours are concerned, an atom of one kind is surrounded by atoms of that same kind. It is evident that this picture represents a statistically average state, and therefore an equilibrium state, i.e. one corresponding to a minimum free energy.

Attempts are sometimes made to describe the phenomenon by means of the ideas and formulae of fluctuation theory, and the formation of clusters is described as a fluctuation. It is obviously understood that the equilibrium distribution under a given set of conditions is a uniform, random distribution of atoms of both kinds.

The following objections may be raised to such a view. In the first place, our picture was derived from X-ray or electron-diffraction data, which reveal *equilibrium* distributions of atoms. Secondly, the probability of a fluctuation increases with temperature according to the formula

$$W_\phi = ce^{-A_\phi/kT}$$

where A_ϕ, the fluctuation energy, is an essentially positive quantity, such that A_ϕ may substantially decrease with increase in temperature. Consequently, the short-range clustering ("stratification") or molecular heterogeneity should increase with temperature if it originated from fluctuations. Experiments show the opposite to be the case. The radial distribution functions for Al–In alloys at two temperatures[2] are shown in Fig. 1. Molecular heterogeneity can be seen to vanish as the temperature is increased: the separation of the first maximum into three peaks decreases

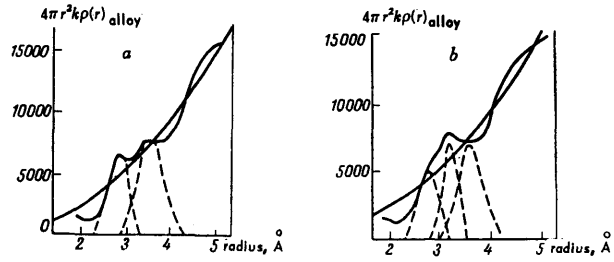


Fig. 1. Radial distribution function for the Al— In alloy: *a*) at 680°; *b*) at 750°.

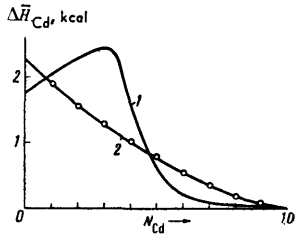


Fig. 2. Partial heat of formation with respect to cadmium in Cd — Pb alloys: 1) at 623°K; 2) at 773°K.

or completely disappears and is replaced by a single maximum which characterises the uniform distribution.

Precisely the same behaviour is observed on studying the thermodynamic properties of systems which form a eutectic in the solid phase. Data for the heat of mixing of liquid alloys of cadmium and lead at two temperatures are reproduced in Fig. 2.

The partial heat of mixing for cadmium at 350°C is a complicated function of composition in no way resembling the curve for regular solutions. At 500° the curve is considerably smoother and has already lost its point of inflection and maximum. Although there are no direct experimental data on the structure of liquid Cd–Pb alloys, we can nevertheless conclude, by analogy with the Al–In alloys, that the smoothing of the $\Delta\bar{H}_{Cd}$ curve results from the disappearance of molecular heterogeneity. Conversely, the complex shape of this curve at low temperatures, near the liquidus temperatures, is definitely connected with the presence of short-range "stratification" or molecular heterogeneity.

Thermodynamic data alone do not establish with complete certainty that molecular heterogeneity of the "stratification" type is present in all liquid alloys that show a more or less extended eutectic field in the solid region of their phase diagram. This is obviously due to the fact that in different systems full miscibility (random distribution of atoms of different kinds) sets in at different temperatures.

For example, the structure of Zn–Sn alloys cannot be unambiguously determined. Practically all liquid alloys of the Zn–Sn system appear to have a completely random distribution of the two kinds of atom. The partial heat of mixing[3] is almost linear. Only in the region of low tin

concentrations is a deviation from linearity observed. The integral heat of mixing gives an asymmetric curve whose maximum is displaced from the 1 : 1 composition to ~0.6 atom fraction of zinc. A similar displacement is also observed with other eutectic systems. The Zn–Sn system can thus be said to exhibit a noticeable, though weak, degree of "stratification".

A completely unambiguous correspondence between the quasi-eutectic structure of the liquid alloys and the thermodynamic properties can be demonstrated with the Pb–Sn system. According to Danilov[4] and Skryshevskii[5] the Pb–Sn alloys show a high degree of inhomogeneity in their short-range order. Thermodynamic studies[6] have shown that the integral heat of mixing of liquid Pb–Sn alloys varies with concentration in the same sense as the heat of formation of solid alloys (Fig. 3). The Pb–Sn phase diagram has two narrow solid-solution fields: lead in tin and tin in lead. Accordingly, the integral-heat-of-formation curve for solid alloys has two branches: one positive, the other negative. The same two branches appear in the heat of mixing curve for liquid alloys. Thus the mode of interaction of lead and tin atoms and the short-range order in their liquid alloys are similar to those in the solid alloys.

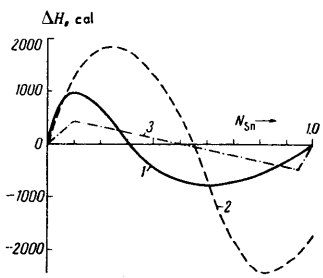


Fig. 3. Heat of formation of Sn — Pb alloys at 1030°K: 1) integral, for liquid alloys; 2) partial, for lead; 3) integral, for solid alloys.

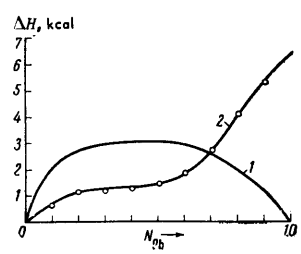


Fig. 4. Heat of formation of Pb — Ag alloys: 1) integral; 2) partial with respect to silver.

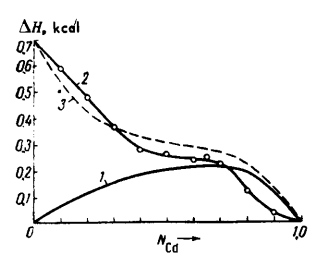


Fig. 5. Heat of formation of Cd — Bi alloys: 1) integral; 2) partial with respect to cadmium; theoretical curve.

The Pb–Sb system exhibits similar thermodynamic properties[7], and its equilibrium phase diagram is analogous to that of the Pb–Sn system. Here, too, we observe two solutions whose heats of formation have opposite signs.

The systems discussed (Pb–Sn and Pb–Sb) form liquid alloys in which the heat of mixing changes sign with change in composition. We shall call them alloys of the first type.

Eutectic alloys have thermodynamic functions of a different type for the liquid state when their phase diagram does not show solid solutions at the two composition extremes.

As mentioned above, the maximum in the integral heat of mixing is displaced towards one of the components and often has the appearance of a sloping plateau. This behaviour is observed especially with Cd–Bi and Ag–Pb alloys. The partial heats of mixing for cadmium and silver in these alloys have a sloping trend in the middle concentration region (Figs. 5 and 4)[8,11,12].

The non-regular concentration dependence of the partial heats of mixing for cadmium and silver can be analytically expressed by an equation, derived by Evseev[11], which involves empirical constants describing the deviations from complete randomness of the distribution of the two kinds of atom.

The partial heat of mixing is given[11] by

$$\Delta\bar{H}_1 = \Delta\bar{H}_\infty \cdot x_2 + \frac{x_1 A x_1 x_2\, e^{-Ax_1x_2/kT} + x_2 B x_1 x_2 e^{-Bx_1x_2/kT}}{x_1 e^{-Ax_1x_2/kT} + x_2 e^{-Bx_1x_2/kT}}, \qquad (14)$$

where $\Delta\bar{H}_\infty$ is the experimentally observed partial heat of mixing, when the first component is infinitely dilute.

The values of the coefficients A and B in Eqn. (14) can be selected on the basis of the activity coefficient at several concentrations. The partial heat of mixing can then be evaluated by substituting these values into the formula.

The calculated and the experimental values of the partial heat of mixing for cadmium in the Cd–Bi system are compared in Fig. 5. The theoretical curve is computed from the equation

$$\Delta\bar{H}_{Cd} = 650\, x_2 + \frac{961 x_1^2 x_2 e^{-0.714x_1x_2} - 1222 x_1 x_2^2 e^{-0.908x_1x_2}}{x_1 e^{-0.714x_1x_2} + x_2 e^{+0.908x_1x_2}}$$

Good agreement is obtained between experiment and theory. It follows that, in general, Eqn. (14) correctly describes the influence of an ordered distribution of atoms on the thermodynamic properties of alloys. However, in some cases the dependence of structure on concentration cannot be limited to the first approximation.

It would be interesting to express the variation of the thermodynamic functions with concentration by substituting into formula (14) experimental data on the structure of the solutions. But one important obstacle arises. In the majority of cases the number of neighbours of the opposite kind, which is needed for calculating the interaction energy in alloys, cannot be evaluated with sufficient precision from diffraction data on the liquid alloys, only general information on the structure of liquid alloys being available.

The absence of a theory of the binding forces in condensed phases (metals, in particular) suitable for practical applications is a further obstacle to the theoretical calculation of the thermodynamic functions of alloys.

At the present time we can only compare thermodynamic

TABLE 1. Coordination numbers for Al—Sn alloys (60% Al).

	n	r_0 Å
Al—Al	10.0	2.70
Al—Sn	1.0	3.05
Sn—Sn	6.2	3.40
Sn—Al	1.5—1.6	3.05

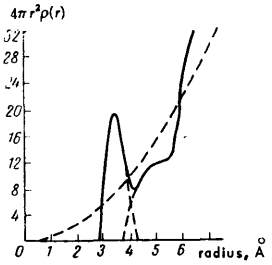


Fig. 6. Radial distribution function for Bi—Pb alloys.

data with an alloy structure on which X-ray and electron-diffraction information already exists. Only a few liquid alloy structures have so far been investigated.

Bublik and Buntar'[12] applied the electron-diffraction method to the study of the structure of liquid Al—Sn alloys. Three maxima, corresponding to the Al—Al, Al—Sn, and Sn—Sn spacings, can be clearly distinguished in the radial-distribution curves for these alloys (see Table 1).

Solid Al—Sn alloys show a wide eutectic region in the phase diagram. In the liquid too, as shown in Table 1, atoms of the same kind are the preferred neighbours, in spite of the fact that a continuous series of liquid solutions is formed. The quantity r_0 in Table 1 is the preferred atom-pair separation in the liquid.

The thermodynamic study of the liquid Al—Sn alloys[13] has not been carried to completion. The work was done at a temperature too high for the effect of molecular heterogeneity on the shape of the heat-of-mixing curve to be pronounced. We can nevertheless observe a shift in the maximum of the ΔH curve, characteristic of eutectic alloys.

Skryshevskii[5] investigated the structure of Bi—Pb alloys of eutectic composition (Fig.6). Danilov and Radchenko[14] had earlier shown qualitatively, from the intensity of scattered X-rays, that atoms of the same kind tend to come together in alloys of eutectic composition. Skryshevskii demonstrated quantitatively that two types of atomic packing exist in eutectic alloys: one with the lead structure and one with the bismuth structure.

The heat of mixing for bismuth-lead alloys[15] does not depart appreciably from regular behaviour, but the partial heat of mixing does, probably owing to the presence of alloys with a quasi-eutectic structure. Partial heats of mixing calculated from formula (14) are in satisfactory agreement with the experimental results. Since formula (14) expresses the functional dependence of the thermodynamic functions on the alloy structure, it follows that we can draw conclusions on the departure of the structure of Bi—Pb alloys from a uniform distribution of atoms of the two kinds by comparing calculated and experimental data.

The Pb—Sn system has been studied by Danilov[16] and, in greater detail, by Skryshevskii[5]. The area under the first maximum of the radial-distribution curve for the eutectic alloy was found to correspond to the sum of the areas for the pure metals. The maximum occurs at r = = 3.26 Å. Consequently, the short-range order in the alloy is similar to that in the pure metals.

However, as already pointed out (Fig.3), the trend of the curve of heat of mixing against concentration for liquid Pb—Sn alloys indicates that structural elements of primary solid solutions are present in the liquid alloys. In other words, not all nearest neighbours are of the same kind as the central atom. It is not possible at the present time to compute the composition of the first coordination shell. This is due to the difficulty of interpreting the experimental data on the structure of liquid alloys and to the low precision with which the area under the maximum of the radial distribution curve can be determined.

Sn—Bi alloys have been studied[17] by electron diffraction. It was found that only with the alloy of eutectic composition could short-range order of the stratification type be demonstrated. All other alloys could be better described by a random distribution of the two kinds of atom.

This is confirmed by the fact that the curve of heat of mixing against concentration has a maximum at the 1 : 1 composition and only a small degree of asymmetry in the direction of bismuth[18]. The system obviously approximates to regularity, both as regards its structure and its thermodynamics, and the small amount of "stratification" at the eutectic composition results from the fact that the structure was studied at a temperature low enough to retain the quasi-eutectic, near the liquidus temperature.

The structure of Zn—Sn alloys was investigated by Lashko[19] at several concentrations, and found to approximate to a completely random distribution of atoms. In no case could the existence of ordering be clearly demonstrated.

The partial heat of mixing for zinc is approximately linear[3] over a wide range of compositions. But the integral-heat-of-mixing curve has a maximum at 0.6, not 0.5 atom fraction of Sn, which denotes non-regularity of the thermodynamic properties of the system.

It should be noted that these departures from the infrequently encountered regular-solution case are not exhibited exclusively by the concentration-dependence of the heat of mixing. Many systems which form eutectics in the solid state have activity coefficients varying with composition in a complicated way. Statistical theory[11] gives the following expression for the activity coefficient in systems comprising two kinds of lattice:

$$\log k_1 = \log\left(x_1 \cdot e^{-(E_{11}-E_{10})/kT} q_{11} + x_2 \cdot e^{-(E_{12}-E_{10})/kT} q_{12}\right). \qquad (15)$$

The variation of the activity coefficient with concentration is therefore determined by the variation of E_{11} and E_{12} with concentration, and therefore also by the structure of the solution or by the short-range order in the atomic distribution (provided that interatomic forces are sufficiently short-range).

Wagner[20] drew attention to the fact that the formulae of the quasi-chemical method do not satisfactorily represent the variation of $\log k_{Cd}$ with concentration in the Cd—Sb system. The same applies to $\log k_{Cd}$ in the Bi—Cd system (Fig.7).

Many eutectic alloys (e.g. Ag—Pb, Pb—Sn, Pb—Sb) have activity coefficients varying with composition in a complicated manner. The concentration-dependence of $\log k$ for

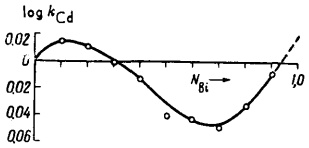


Fig. 7. Concentration dependence of the activity coefficient of cadmium in the Bi — Cd system.

these alloys may be satisfactorily described by assuming the same approximate variation with concentration of E_{11} and E_{12} as in the calculation of the partial heat of mixing.

Consideration of the currently available data on the structure of liquid alloys in conjunction with the thermodynamic properties of these alloys thus leads to the conclusion that the structure in general corresponds with the thermodynamic properties. The statistical theory of solutions, based on a specific model of their molecular structure, can reveal the link between the two approaches. However, there are not sufficient data for a theoretical calculation of the thermodynamic properties of liquid alloys, and furthermore the determination of the structure of liquid alloys still presents grave difficulties.

In conclusion, mention may be made of the so-called positive and negative deviations of the activity from Raoult's law. Negative deviations of the activity from the atom fraction are very often said to denote the presence of intermetallic compounds in the liquid phase or the formation of atomic groupings of the intermetallic compound type. Positive deviations, on the other hand, are ascribed to a tendency of the solution towards stratification. This incorrect opinion is expressed by several authors, who base their views on the early publications of Taylor[21] and Wagner[22].

By comparing the $\log k$ curves for the Cd–Bi and Sn–Pb systems with the data on the structure of these eutectic alloys we find that the activity of the components can exhibit either positive or negative deviations from Raoult's law if the system tends towards stratification. These deviations are induced by an ordered structure of a single type: stratification. It is only possible, therefore, to judge whether the ordering of the structure belongs to the "stratification" or to the "compound formation" type on the evidence of a complete analysis of the thermodynamic data, based on formulae such as (14) and (15).

Conclusions about the structure of a solution should on no account be considered reliable if they are derived merely from the variation of activity with concentration.

2. LIQUID ALLOYS OF SYSTEMS WITH COMPOUNDS IN THE SOLID PHASE

It is desirable to compare the data on the structure of liquid alloys which form one or more compounds in the solid phase with the corresponding thermodynamic parameters. The compounds may be either of the berthollide or of the daltonide type. Starting from the general proposition, put forward by Danilov[4], of corresponding solid- and liquid-alloy structures, we can suggest that order of the "compound-formation" type exists in both liquid and solid alloys, i.e. that as far as short-range order is concerned the structure of the liquid alloys is similar to that of the compound in the solid phase.

In the Au–Sn system the solid-phase compounds AuSn, $AuSn_2$, and $AuSn_4$ can be distinguished. Skryshevskii[5] and Hendus[23] made X-ray studies of the structure of liquid alloys of composition AuSn. It was found that each Sn atom is surrounded by 6.5 atoms of Au, and the Au atom is also surrounded by 6.5 Sn atoms. These experiments were carried out at 450°, i.e. near the liquidus temperature.

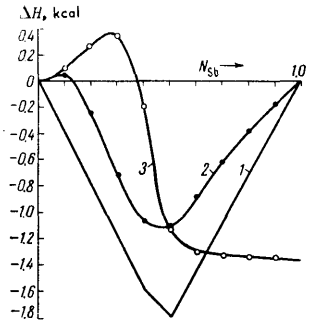


Fig. 8. Heat of formation of Cd — Sb alloys: 1) integral, for solid alloys; 2) integral, for liquid alloys; 3) partial with respect to Cd.

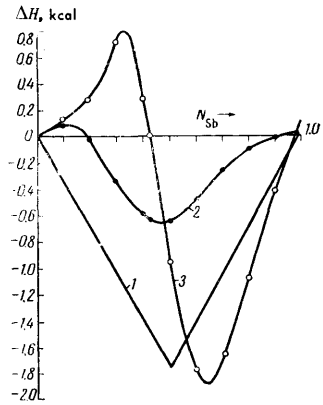


Fig. 9. Heat of formation of Zn — Sb alloys: 1) integral, for solid alloys; 2) integral, for liquid alloys; 3) partial with respect to Zn.

The atomic distribution found for the liquid alloy corresponds to that for the solid alloy of the same composition. Clearly, as in the case of eutectic alloys, the given atomic distribution is only an approximation to the actual state of affairs. A fraction of the Sn atoms may exchange places with Au atoms. Available structural data are insufficient for a precise calculation of the number of nearest neighbours of the two kinds.

The heat of mixing for Au–Sn alloys has been measured[24] at 550°, and does not reveal any departures from regularity. This is hard to explain, especially since a number of alloys of the same type give quite appreciable effects. Kleppa[24] found that the entropic contribution of Sn at 550° shows a peculiar concentration-dependence, which Frost attributes[25] to ordering processes in the liquid phase.

Solid alloys of the Cd–Sb system are characterised by the presence of the compounds CdSb and Cd_3Sb_2. No structural studies of the liquid alloys of this system have been published, but one can nevertheless expect to find short-range order in them by analogy with the Au–Sn system.

By comparing the thermodynamic data[26,27] for the solid and liquid alloys (Fig.8) we can conclude that the solid and liquid structures are of a similar character. The heat of formation of the liquid alloys at the eutectic composition is positive. The subsequent trend of the heat-of-mixing curve is surprisingly reminiscent of the heat-of-formation curve for the solid alloys. It follows that short-range order of the "compound-formation" type exists in the liquid alloys.

In the Zn–Sb system there are three compounds of composition between 0.5 and 0.6 atom fraction of zinc. The heat of formation of the solid alloys at 20°, and the integral heat of mixing for the liquid alloys, are shown in Fig.9. Once again we find that the concentration dependence of the heats of formation of solid and of liquid alloys shows similar trends. The structure of the solid and liquid alloys can therefore be said to be very similar within the limits of short-range order. No structural investigations of liquid Zn–Sb alloys have been reported.

The peculiar variation with concentration of the partial heat of mixing for zinc and cadmium is noteworthy. The sharp inflection of $\Delta\bar{H}_{Cd}$ in the region of the compounds indicates a reorganisation of the structure of one of the "microphases", or, to put it differently, of a cluster-like heterogeneity of molecular dimensions; this is similar to what takes place in the solid.

The behaviour of the heats of formation of liquid and of solid alloys in the Bi–Mg system[29,30] is analogous to those discussed above. The formation of the compound Mg_3Bi_2 in the solid phase can be recognised by a maximum in ΔH at a composition corresponding to a 3 : 2 ratio. The same maximum can be observed, at the same composition, with liquid alloys. The partial heat-of-mixing curve for magnesium shows an inflection, also at the 3 : 2 ratio. One must therefore presume that a structural correspondence between liquid and solid alloys exists in the Mg–Bi system.

The solid compounds Mg_3Bi_2 and Mg_3Sb_2 have the same type of structure. Accordingly, their thermodynamic functions are similar. The integral and the partial heats of formation of the Mg–Sb alloys therefore vary with concentration just like the corresponding quantities for the Mg–Bi system[27,31].

The curves of the thermodynamic functions of the Mg–Sb system retain the same general appearance for the liquid state as for the solid state. Hence we can conclude that the liquid and the solid state structures for the Mg–Sb system are similar.

The Mg–Pb and Mg–Sn systems are no less interesting than the two systems just discussed. They form the solid compounds Mg_2Pb and Mg_2Sn which, like the bismuth and antimony compounds of magnesium, are valence-bond compounds and have an antifluorite-type lattice.

A review of the thermodynamic properties[13,15,28,29] of these compounds once again confirms that similarity in the liquid and solid states is maintained and provides undeniable evidence of the closeness between the structures of the two states. The variation of the activity coefficient with concentration is complex: an inflection at about 0.6 atom fraction of magnesium denotes a transformation of the structure with change in concentration. This yet again underlines the existence of order of the "compound-formation" type in the liquid alloys.

3. ORDERING PROCESSES IN SOLID SOLUTIONS

Structural studies on various alloys led to the discovery of the phenomenon of ordering in solid solutions. There is no experimental criterion for identifying alloys capable of forming ordered solutions. Not all solid solutions are able to undergo ordering.

Ordering is detected by the appearance in the X-ray diffraction pattern of "superlattice" lines, additional to the lines given by a pure metal with the same lattice. The formation of a superlattice in the Au–Cu alloy having a 1 : 1 ratio of components is a simple example of ordering.

The copper-gold solid solution has a face-centred cubic lattice whose lattice sites can be occupied by any atom with equal probability. When the temperature is lowered it becomes energetically more favourable to let the nearest-neighbour sites surrounding any atom be occupied by atoms of the opposite kind. From the point of view of the quasi-chemical theory of solutions[31] the phenomenon is described by the condition

$$V_{AB} < {}^1/_2(V_{AA} + V_{BB}),$$

where V is the atomic interaction potential. In the cell method the same condition is formulated as follows:

$$E_{11} < E_{12},\ E_{22} < E_{21},$$

where E_{ij} is the energy of the i-th atom in the j-th cell.

As a result, the structure of the solid solution suffers a reorganisation such that each copper atom is surrounded by gold atoms only, and each gold atom by copper atoms only. In the case of AuCu the original solid-solution lattice is not retained: a transformation from the cubic to the face-centred tetragonal form takes place. When the $AuCu_3$ alloy becomes ordered, on the other hand, the lattice of the solid solution

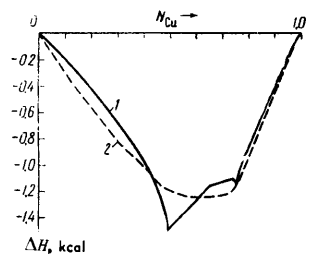


Fig. 10. Integral heat of formation of Cu–Au alloys: 1) below the ordering temperature; 2) above the ordering temperature.

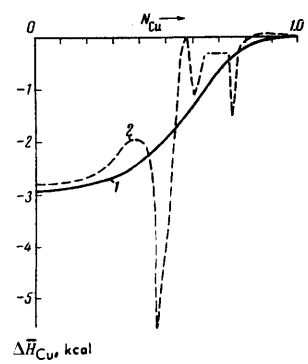


Fig. 11. Partial heat of formation of Cu–Au alloys with respect to Cu: 1) above the ordering temperature; 2) below the ordering temperature.

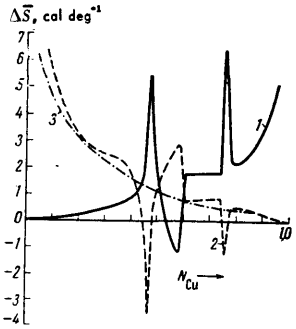


Fig. 12. Partial entropy of formation of Cu–Au alloys: 1) with respect to Au; 2) with respect to Cu; 3) with respect to Cu, above the ordering temperature.

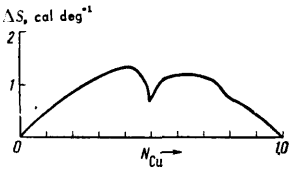


Fig. 13. Integral entropy of formation of Cu–Au alloys below the ordering temperature.

is preserved with only a slight change in dimensions.

It should be mentioned that small heterogeneous fields lie adjacent to the homogeneous fields of the ordered solutions in the phase diagram for the system; the type of the order–disorder phase transition is thus defined.

Bragg and Williams's first statistical theory[32,33] classifies order–disorder changes in alloys among phase transitions of the second kind, which are characterised by a finite jump in heat capacity. But in a transition of the second kind the continuous change in thermodynamic properties with temperature does not admit the existence of heterogeneous regions. Landau[34] showed that the change in lattice symmetry which accompanies phase transitions of the second kind must be taken into account. From the point of view of statistical theory the order–disorder transformation is a mixed phase transition of the first and the second kinds with a continuously changing probability of finding atoms of the two types at their "proper" or at "foreign" lattice sites. Let us now turn to the thermodynamics of copper-gold alloys undergoing ordering.

Oriani[35], and Weibke and Quadt[36], studied the thermodynamic properties of ordered Cu–Au alloys by the e.m.f. method. The heats of formation of Cu–Au alloys at 380° are given in Figs.10 and 11. Alloys of compositions 1 : 1 and 1 : 3, corresponding to CuAu and Cu_3Au, give rise to maxima in the heat-of-formation curve, similar to those accompanying the formation of intermetallic compounds. The main dissimilarity is the absence of an appreciable region, near the ordering composition, over which ΔH varies linearly with concentration.

The variation with concentration of the partial and the integral entropies below the ordering temperature has a characteristic form in the Au–Cu system (Figs.12 and 13). The partial-entropy curves for copper and gold change in the opposite sense in the region of concentrations investigated. The peaks in the partial-entropy curves (Fig.12) obviously define the concentration limits within which ordering can proceed. For ordered solution near $N_{Cu}:N_{Au}$ = = 1 : 1 the curves of $\Delta\bar{S}_{Au}$ and $\Delta\bar{S}_{Cu}$ change smoothly, probably in proportion to the degree of long-range order.

The curve of the change in integral entropy with concentration (Fig. 13) exhibits a minimum at a 1 : 1 ratio, connected with the decreased entropy of formation of this alloy, as required by statistical theory. The "configurational" entropy of formation of the fully ordered alloy is zero. At 380°, near the onset of disorder, both the configurational and dynamic distortions, or fluctuations, of the positions of the atoms become large.

The concentration variation of the thermodynamic properties of the Cu–Au system in its ordered condition depends on the alloy structure. The type of variation can be explained by statistical theory provided that the structure of the alloys is taken into account.

Ordered solid solutions in the Cu–Pt system have also been fairly thoroughly studied from the thermodynamic point of view. Here, too, ordered solutions with compositions CuPt and Cu_3Pt are formed. Johanson and Linde[37] studied the structure of Cu–Pt alloys and found a face-centred cubic lattice for disordered solid solutions. Ordered alloys of composition Cu_3Pt have also the same lattice.

In the region of 40–55 at.% Pt a rhombohedral structure, resulting from the deformation of a cubic lattice, is imposed by the appearance of order. Between 60 and 75 at.% Pt a cubic lattice with an ordered distribution of atoms is formed. The partial and the integral entropies[38] of formation of the alloys are analogous to those of the Cu–Au system in their concentration dependence. The integral heat of formation of the Cu–Pt alloys also shows the two characteristic maxima at the atomic ratios 1 : 1 and 1 : 3 respectively.

We can postulate that short-range order exists above the ordering temperature in the solid solutions of the Cu–Au and Cu–Pt systems which undergo ordering, since the nature of the forces of atomic interaction hardly changes above the ordering temperature. Short-range order in ordered solid solutions implies that in the preferred atomic distribution neighbouring atoms are of different kinds. This ordering phenomenon is formally similar to that which takes place in liquid alloys when eutectics or intermetallic compounds occur in the solid phase.

Roberts[39] and Cowley[40] have studied experimentally the short-range order in Cu–Au alloys above the ordering temperature. Table 2 shows some experimental values of the short-range order parameter α_i for several of the innermost shells surrounding a chosen central atom.

The number of Cu atoms in the i-th coordination shell of an Au atom may be determined as follows. Take the first shell, for instance:

$$\alpha_1 = 1 - \frac{n_{Cu}}{m_i x_{Cu}} = 1 - \frac{n_{Cu}}{12 \times 0.5} = -0.133.$$

The required value, $n_{Cu} = 12 \times 0.5 \times 1.133 = 6.8$, can be easily derived. If perfect short-range order existed in the first shell, n_{Cu} would be 8, and therefore α_1 would be -0.33; at the opposite extreme of complete disorder $n_{Cu} = x_{Cu} \times 12 = 6$, and consequently

$$\alpha_1 = 1 - \frac{6}{12 \times 0.5} = 0.$$

TABLE 2. Data for single-crystal Cu—Au alloys.

Coordination shell i	Coordination number m_i	α_i complete order	α_i 425°
1	12	—0.33	—0.133
2	6	1.00	—0.065
3	24	—0.33	0.020
4	22	1.00	0.066
5	24	—0.33	—0.033
6	8	1.00	0.035

TABLE 3. Short-range order parameters for Cu—Pt alloys.

Coordination shell	Complete order: number of like neighbours	Complete order: number of unlike neighbours	α_{id}	α_{exp} (890°)
1	6	6	0	0.00
2	0	6	—1	—0.20±0.06
3	12	12	0	0.00
4	12	0	1	+0.12±0.05

These experimental data provide a clear picture of short-range order in Cu—Au alloys above the ordering temperature. This type of order changes smoothly with concentration, unlike long-range order below the ordering temperature. Therefore, the thermodynamic functions of solid solutions are also smooth functions of concentration.

The partial and the integral heats of formation of copper-gold solid solutions are displayed in Figs. 10 and 11. The general trend of the variation of the integral heat of formation with concentration corresponds to that for the ordered condition. The partial-heat-of-formation curve for copper (Fig. 11) shows a characteristic inflection at the 1 : 1 composition.

Inferences as to the effect of short-range ordering on the thermodynamic functions of the Cu—Au alloys may also be drawn from the variation of the excess entropy for copper with concentration. A minimum at the 1 : 1 composition, clearly related to short-range order, can be observed in the curve.

Short-range order in Cu—Au alloys also affects the way in which the activity coefficient varies with concentration. $\log k$ for copper as a function of concentration has a trend similar to that of the partial heat of formation of the alloy with respect to copper. If we remember that

$$\log k = \frac{\Delta\bar{H}}{2.3\,RT} - \frac{\Delta\bar{S}_{excess}}{2.3\cdot R},$$

the similarity becomes easy to understand. The heat of formation of the alloy provides the major contribution to the departure of the activity from the concentration.

Short-range order has also been studied[41] in copper—platinum alloys at 890°, i.e. above the ordering temperature. Table 3 gives experimental values for the short-range-order parameter.

As in the case of Cu—Au alloys, short-range order is again observed. It is interesting to note that the partial heat of formation with respect to copper shows a clearly defined plateau over a wide range of concentrations, bearing a slight resemblance to the inflection in the corresponding curve for the Cu—Au alloys. In both the copper-rich and the platinum-rich regions the curve coincides with that for the ordered condition: this can be explained if the primary solutions have a similar character above and below the ordering temperature. In view of the fact that short-range order is experimentally established, the practically constant partial heat of formation in the middle region of the curve must be ascribed to ordering. The dependence of the thermodynamic functions of the alloys on short-range order is thus observed for solid as well as for liquid solutions.

Similar relationships between thermodynamic properties of the solid solutions and structure are again found in the Mg—Cd system. Short-range order has not been experimentally studied in these alloys, and neither have the thermodynamic properties of the ordered solid solutions. For the disordered solutions, however, the thermodynamic properties are known[42]. Their dependence on concentration is analogous to that for the Cu—Au system. Since long-range order is observed in the Cd—Mg system, the similarity in properties between the Cu—Au and the Cd—Mg alloys must be ascribed to the influence of short-range ordering.

Dehlinger[43] studied the structure of the ordered Cd—Mg alloys, $CdMg_3$ and Cd_3Mg. The two series of solid solutions (α and β) in the Mg—Cd system have lattices with hexagonally close packed magnesium and cadmium atoms at all concentrations (axial ratio c/a 1.89 and 1.62 respectively); the lattice dimensions decrease as the concentration of the second component increases. Below 253° superlattices are observed. Alloys of compositions Cd_3Mg and $CdMg_3$ have the cadmium and the magnesium lattice respectively, but with an ordered distribution of atoms. Alloys near the composition CdMg also appear to have the Mg and Cd lattices.

A striking similarity between the alloys of the Cd—Mg and the Au—Cu systems above the ordering temperature is revealed by comparing their heat-of-formation-curves. The partial heat of mixing for Mg shows the same trend with concentration as $\Delta\bar{H}$ for copper in the Cu—Au system (Fig. 11). Consequently, by analogy with the Cu—Au system, we can suggest that short-range order is also present in the Cd—Mg alloys above the critical temperature.

It would be wrong to assume that short-range order exists only in those cases in which long-range order is observed below a critical temperature. The appearance of short-range order in the distribution of atoms is caused by binding forces, and these are so general that the above warning applies to any alloy, whatever the type of interatomic force. Thus, short-range order can be detected experimentally in Ag—Au alloys[44], in which no long-range order has been observed. Data on the number of nearest neighbours in solid Ag—Au alloys, obtained by measurements of diffuse X-ray scattering, are presented in Table 4.

Short-range ordering is also observed in α-brass[45]. The "stratification" type of ordering, which is detected in the solid as well as in the liquid alloys, is more frequently referred to as grouping of like atoms. This phenomenon has

TABLE 4. Short-range order in Ag—Au alloys at 400° (quenched).

Composition	Short-range order parameter α_i	Number of nearest-neighbour Ag atoms around each Au atom
AgAu	$\alpha_1=-0.080$ $\alpha_2=+0.01$	6.48
Ag_3Au	$\alpha_1=-0.05$ $\alpha_2=+0.01$	9.45

been studied experimentally in the solid solutions of the Al—Zn and Al—Ag systems.

Guinier and Walker[46] studied the short-range order in the Al—Ag alloy containing about 6 at.% Ag in the field of the δ-phase. At 500° this field appears as a solid solution. Below 450° segregation of the γ-phase takes place. We can therefore expect ordering in these alloys to be of the "stratification" type, i.e. that regions rich either in silver or in aluminium will appear.

The silver-rich microscopic regions of the alloy proved to have a diameter of 16 Å, the aluminium-rich micro-regions 72 Å. These results apply in particular to the partly annealed alloys, at different stages of segregation of the γ-phase, but we can assume that ordering is preserved at high temperatures even though no precise experimental proof exists. The available thermodynamic data for the δ-phase of the Al—Ag system[47] are too scanty to illustrate the effect of short-range ordering of the stratification or grouping type.

The presence of short-range order in alloys is of more frequent occurrence than its absence. This affects not only the thermodynamic properties of the alloys but also several other physical properties. This is why it is so important to establish the connection between the thermodynamic properties and the atomic structure of alloys; this may lead to the development of a statistical theory of alloys, essential for the prediction of alloy properties.

The phenomenon of ordering, as shown above, can in general be subdivided into two types: "stratification" and "compound formation". This applies equally to the liquid and to the solid solutions. The observed direct link between short-range order in liquid solutions and the structure of the corresponding solids confirms Danilov and Radchenko's hypothesis of congruent structures of liquid and solid alloys.

A combined analysis of the thermodynamic and structural data for liquid alloys can throw light on the correctness of the cellular statistical theory, the basis of which was first laid by Frenkel'[48]. According to this theory, atoms in the liquid spend the greater part of their time in vibrational motion within "cells" made up of other atoms, just like atoms in a solid. The introduction of the concept of two kinds of cells[11] gives greater precision to the cellular model of liquids and links the thermodynamic data with the structural data for the liquid.

Eutectic alloys give quasi-eutectic liquid solutions; alloys forming compounds give liquids in which the atomic packing is not very different from the short-range order found in intermetallic compounds. "True" solutions, in which the atoms of both kinds are distributed completely at random, are rarely encountered, and then only if the temperature is sufficiently high.

Ordering is also observed in solid solutions. The thermodynamic functions of these alloys, like those of the liquids, exhibit a characteristic concentration dependence, reflecting the effect of short-range order in the atomic distribution, since these functions appear to be very sensitive to the pattern of nearest neighbours.

The concept of the short-range order includes the number of atomic neighbours not only in the first coordination shell but also in the second and the third. It has not yet proved possible to carry out a precise evaluation of the contribution of these atoms to the interaction energy, but their influence is nevertheless considerable.

In the present review the discussion of structure has been mainly confined to short-range order in the atomic distribution in alloys, both liquid and solid. This seemed justified in view of the importance of short-range order, which can throw light both on the crystallisation of liquid metals and on stabilising (hardening) processes in solid solutions.

Dispersion hardening of alloys is known to be related to their submicroscopic heterogeneity; the interaction of dislocations with atomic agglomeration can be considered as a factor in the stabilising (hardening) process.

From the point of view of statistical theory short-range order also plays an important part in determining the thermodynamic properties of alloys.

It is evident that no further progress towards a complete elucidation of the link between the structure and the thermodynamics of alloys is possible unless long-range order is taken into consideration. Such a wide view of the problem, however, would go beyond the terms of reference of a single review article. The restricted scope of the present review is therefore not entirely arbitrary.

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SOME REACTIONS OF NITRILES WITH THE FORMATION OF A NEW NITROGEN–CARBON BOND

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INTRODUCTION

Since the nitrogen atom is more electronegative than the carbon atom, the negative charge in nitrile molecules is displaced towards the former. The triple bond in the nitrile group is made up of one σ-bond and two π-bonds, and since a π-bond is more polarised than a σ-bond, nitrile molecules are particularly polar. In fact, with the interatomic distance in the nitrile group of 1.15 ± 0.02 Å [1,2], the dipole moments of aliphatic nitriles are 3.44–3.65 *D* in solution[3] and 3.94–4.09 *D* in the vapour phase[4]. The considerable polarity of the nitrile group is the cause of its ability to enter into addition reactions:

$$-\overset{\delta+}{C}\equiv\overset{\delta-}{N}$$

Moreover, as Newman pointed out[5], addition to the nitrile triple bond is less dependent on steric factors than addition to the double bond in carbonyl and other compounds.

The review literature has been mainly concerned with the reactions of nitriles with nucleophilic reagents (hydroxylamines, hydrazine, ammonia, etc.)[6]. The Hoesch synthesis, in which the nitrile group reacts in the presence of hydrogen halides to form a carbon–carbon bond, has been reviewed[7,8]. The preparation of iminoether hydrohalides (the formation of a carbon–oxygen bond) by the reaction of the nitrile group with alcohols and hydrogen halides was the subject of a large monograph[9] and has been treated in many reviews[7,10]. The literature on the Stephen reaction (the synthesis of aldehydes from nitriles in the presence of hydrogen chloride and stannous chloride) has been collated[11].

However, the reactions of the nitrile group involving the formation of a nitrogen–carbon bond has received very little attention in the review literature. Migrdichian's book "The Chemistry of Organic Cyanogen Compounds" contains only one chapter on this subject, relating to the polymerisation of nitriles[7]. Other reactions, particularly those discovered in the last 10–15 years, are barely mentioned in reviews.

The present review is an attempt to fill this gap, and is concerned with those reactions of nitriles in which a new nitrogen–carbon bond is formed, catalysed by protonic or Lewis acids.

The electrophilic reactivity of nitriles has never been in doubt. Remick[12] considered that since the tendency of the carbon atom, with a deficit of electrons, to accept electrons is greater than the tendency of the nitrogen atom, with an excess, to make these available, nitriles must possess predominantly electrophilic reactivity, but he supposed that they may also show nucleophilic properties. The considerable experimental and theoretical material accumulated since

the publication of Remick's book (1945), shows clearly that reaction at the nucleophilic nitrogen atom is important. The nucleophilic character of the nitriles is caused by the presence in the $-C\equiv N$ group of an unshared electron pair and the electron-donating π-bonds. The nucleophilic properties of nitriles are shown by the formation of molecular compounds with electrophilic reagents (see, for example, Tronov and Strel'nikova[13]). The addition of such reagents to the electron pair of the nitrogen atom of the nitrile group usually gives molecular compounds containing equivalent amounts of both substances. It has been suggested[14] that the addition to a nitrile of more than one equivalent of an electrophilic substance is due to the formation of so-called π-complexes.

The part played by acids in nucleophilic reactions of nitriles is primarily due to their increasing the electrophilic properties of the reagents reacting with the nitriles. The acid and the electrophilic reagent may form a carbonium ion by one of the following reactions:

$$RX + A \rightleftarrows R^+ + AX^-,$$
$$R_1 + HB \rightleftarrows R_1H^+ + B^-.$$

In the first reaction a protonic or Lewis acid (e.g. $AlCl_3$) reacts with the negative substituent X of the reagent RX (e.g. an alkyl halide or alcohol) to form a carbonium ion and an anion (e.g. $AlCl_4^-$). In the second reaction the hydrogen acid HB increases the electrophilic properties of compounds such as olefines or ketones and aldehydes (R_1) by protonating them.

The resulting carbonium ions then react with the unshared electron pair of the nitrile nitrogen, or, what is equivalent, with the π-electrons of the triple bond:

$$R'C\equiv\overset{\curvearrowright}{N}{+}R^+ \longrightarrow [R'C{=}NR]^+$$

The new cation, in which the positive charge is concentrated on two atoms (the nitrogen and the carbon), can be stabilised by the anion present in the reaction mixture, or can react with the solvent or any other nucleophilic substance, for instance:

$$[R'C{=}NR]^+ + AX^- \rightarrow R'C\begin{matrix}NR\\ \diagup\\ \diagdown\\ X\end{matrix} + A.$$

It is understood that the above schemes, like most of those used in this review, must be considered only as models of the more complex conversions which actually occur. In particular, the acids can react with compounds which act as electron acceptors in the reactions with the nitriles to form strongly electrophilic molecular compounds instead of cations[15]. Complete conversion to the nitrilium salt need not take place. It is possible that the addition of the electrophilic and nucleophilic components to the nitrile group takes place in one stage with the formation of a single transition state. However, the main scheme of nucleophilic reactions of nitriles is not changed by this.

Work on *N*-substituted nitrilium salts recently prepared by Meerwein[16] supports the above scheme. *N*-Alkyl and *N*-aryl nitrilium salts react chiefly by addition to the electrophilic carbon atom. With water they give *N*-substituted amides, with alcohols iminoethers, with amines amidines, and so on.

$$[R'C\overset{\curvearrowleft}{\equiv}\overset{\curvearrowright}{N}R]^+X^- + H\ddot{O}C_2H_5 \longrightarrow \underset{\ddot{O}C_2H_5}{RC{=}\ddot{N}R} + HX$$

The structure of the nitrilium salts has been confirmed spectroscopically[17]. The reaction of the nitrilium salts with nucleophilic molecules or ions to form new nitrogen–carbon bonds (as well as the existence of these salts) confirms that the nucleophilic reactions of nitriles can take place by the above scheme.

We begin the review of reactions of nitriles as nucleophilic agents with a description of the nitrilium salts and their reactions. Other sections (3–7) are concerned with other reactions of nitriles as nucleophilic reagents (the synthesis of bis-amides from nitriles and aldehydes, the synthesis of *N*-substituted amides by the Ritter and analogous reactions, the polymerisation of nitriles to symmetrical triazines, etc.) which take place in acid medium or in the presence of acid catalysts. Probably in most of these there is direct reaction between the nitrile nitrogen and the electrophilic carbon.

As regards the polymerisation reactions of nitriles, the formation of the new nitrogen–carbon bond is achieved by the simultaneous appearance of nucleophilic and electrophilic reactivity in the nitrile group, as will be shown in section 6.

Nitriles can take part in the formation of a new nitrogen–carbon bond by sharing the electron pair of the nitrile nitrogen with a carbon atom of the electrophilic reagent, and also by other reactions. These include acid-catalysed reactions in which nitriles react as electron accepting substances, with the formation of a new carbon–oxygen bond. The nitrogen–carbon bond then arises by intramolecular rearrangement of the resulting compound. In these reactions the acids, by reacting with the nitrile nitrogen, cause a decrease in the electron density on the carbon atom of the $C\equiv N$ group and so increase its electron accepting properties, e.g.:

$$RC\equiv N + HB \rightleftarrows [RC{=}NH]^+ + B^-.$$

This group of reactions includes the synthesis of imides from nitriles and carboxylic acids (section 8) where the nitrogen–carbon bond arises by the rearrangement of the *O*-acyl compounds to the *N*-acyl compounds.

It should be noted that the considerations given above are insufficient to explain the mechanism of certain of the reactions reviewed here. The corresponding sections of the review will indicate the possibility of the reactions taking place by other mechanisms.

1. *N*-SUBSTITUTED NITRILIUM SALTS

Recently Meerwein and his coworkers[16] have developed methods for the preparation of stable nitrilium salts of the general formula $[RC{=}NR']^+X^-$, where R is alkyl or aryl, R' is alkyl, aryl, or acyl, and X^- is an anion. The *N*-alkyl nitrilium salts are formed by the reaction of aliphatic or aromatic nitriles with trialkyloxonium salts of complex halogenoacids:

$$C_6H_5CN + [(C_2H_5)_3O]^+AlCl_4^- \rightarrow [C_6H_5C{=}NC_2H_5]^+AlCl_4^- + (C_2H_5)_2O.$$

Fluoroborates and hexachloroantimonates can also be prepared by this method. Another method which has been suggested for the preparation of *N*-alkyl nitrilium salts is the reaction between alkyl halides and the molecular compounds of nitriles with metal chlorides, for example:

$$CH_3C\equiv\overset{+}{N}\cdot\bar{S}bCl_5 + C_2H_5Cl \rightarrow [CH_3C{=}NC_2H_5]^+SbCl_6^-.$$

The rate of addition in this reaction decreases in the series tertiary > secondary > primary alkyl chloride. The molecular compounds of nitriles with ferric chloride, aluminium chloride, and stannic chloride add alkyl halides

less readily than the compounds with antimony pentachloride.

Acyl chlorides add to the molecular compounds of nitriles with electrophilic metal chlorides analogously to the alkyl chlorides, forming salts which usually contain at least two molecules of nitrile for each acyl chloride molecule.

The above reactions are not applicable to the preparation of *N*-aryl nitrilium salts. These are easily obtained by the reaction of electrophilic metal chlorides with *N*-aryl iminochlorides [16,18]:

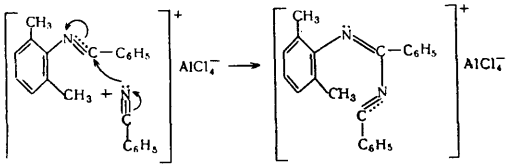
$$RC(=NR')Cl + TiCl_4 \rightarrow [RC{\equiv}NR']^+ TiCl_5^-.$$

Another method is based on the reaction of aryl diazonium fluoroborates with aliphatic and aromatic nitriles:

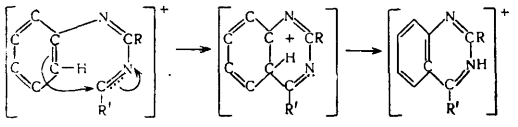
$$[R'N{\equiv}N]^+ BF_4^- + RCN \rightarrow [RC{\equiv}NR']^+ BF_4^- + N_2.$$

This synthesis was developed by Meerwein [16]. However, it had already been shown that *N*-aryl nitrilium salts are intermediates in the formation of substituted amides in the reaction of nitriles with diazonium salts [19,20].

The nitrilium salts can also add on a second molecule of nitrile [21]:

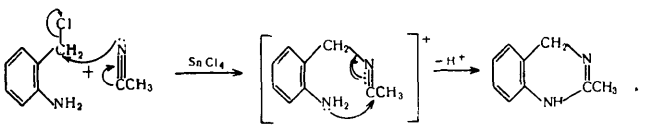


The same product is obtained by the reaction of *N*-aryl iminochlorides with the molecular compounds of nitriles and electrophilic metal chlorides. These new nitrilium salts correspond to the products of composition 2RCN.HCl described by Grundmann and coworkers [22] (see section 6). Nitrilium salts containing two nitrile molecules can only be obtained (as the above equation indicates) when the *o*-positions of the *N*-aryl group are substituted. In the presence of *o*-hydrogen atoms, intramolecular condensation occurs, with electrophilic substitution in the benzene nucleus, forming quinazolinium salts. On treatment with alkali these are converted to quinazolines:

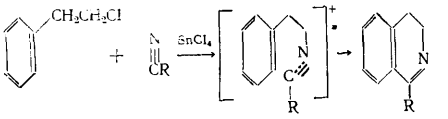


The quinazoline synthesis is simplified if it is combined with the preparation of the substituted iminochlorides. For example, heating a solution of benzanilide in benzonitrile with thionyl chloride and aluminium chloride produces 2,4-diphenylquinazoline in good yield. Iminoethers may be used instead of the substituted iminochlorides in the synthesis of quinazolines.

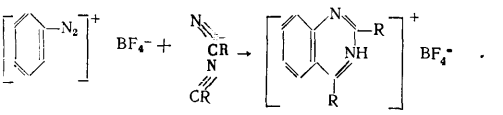
2-Methyl-1,4-dihydroquinazoline has been prepared from *o*-(chloromethyl)anilinium chloride, acetonitrile, and stannic chloride, by an intramolecular reaction in the nitrilium ion [23]:



Intramolecular reaction also results in the formation of 3,4-dihydroisoquinolines by heating equimolecular quantities of β-chloroalkylbenzenes and the complexes of stannic chloride with nitriles [23]:



Quinazolinium salts are also formed when aryl diazonium tetrafluoroborates or other diazonium salts are heated with nitriles [21]:



2. PREPARATION OF BIS-AMIDES BY REACTION OF NITRILES WITH ALDEHYDES

In 1876 Hepp and Spiess [24] showed that at room temperature the reaction of aliphatic aldehydes with benzonitrile in the presence of excess concentrated sulphuric acid produces bis-amides:

$$RCHO + 2\,C_6H_5CN + H_2O \rightarrow RCH(NHCOC_6H_5)_2.$$

This reaction was later carried out with benzyl cyanide [25,26] and a number of other compounds [27,28]. Comparatively recently it was found [29,30] that aliphatic nitriles also condense with aliphatic aldehydes. Methylene-bis-vinylacetamide has been prepared from allyl cyanide and paraformaldehyde in the presence of 85% phosphoric acid at 60° [31]. Sulphuric acid produces benzylidene-bis-acetamide from acetonitrile and benzaldehyde [32]. Formaldehyde has been used as the bisulphite compound for condensation with benzonitrile [26].

It is clear [33] that nitriles react smoothly only with those aliphatic aldehydes which do not contain α-hydrogen atoms. Under the reaction conditions, aldehydes with α-hydrogen atoms generally undergo autocondensation. Chlorosulphonic and other acids may be used as catalysts in place of sulphuric and phosphoric acids. Mixtures of sulphuric with acetic [25] or formic [33] acid are also used; the reaction temperature must not exceed 30°–50°. If formic acid alone is used as catalyst, the temperature must be raised to 100° [33].

Hydrogen chloride also influences the condensation of aldehydes with nitriles favouring formation of bis-amides [34,35]. A bis-amide is formed by passing hydrogen chloride into an ethereal solution of an aliphatic nitrile [36] or benzoylmandelonitrile [37] and an aromatic aldehyde and subsequently treating with water. A variation of this method, recently

patented[38], comprises passing hydrogen chloride into a mixture of nitrile, formalin, and concentrated hydrochloric acid.

Under the conditions of the Stephen reaction (passing hydrogen chloride into an ethereal solution of a nitrile in the presence of stannous chloride) certain aliphatic nitriles have produced bis-amides, apparently formed by condensation of the nitriles with their products of hydrochlorination[39]. The patent literature describes the catalytic vapour-phase preparation of bis-amides from aliphatic aldehydes and aliphatic or aromatic nitriles[40] (including halogen- and carboxyl-substituted mononitriles[41,42]) in the presence of water and hydrogen halides, formic acid, or acetic acid. The optimum temperature is 350°–380°, with a catalyst containing boron phosphate and alumina or other acidic compounds. For example, methylenebis(α,β-dibromopropionamide) has been obtained from acetaldehyde and α,β-dibromopropionitrile[41]. ω,ω'-Substituted bis-amides can be used to prepare high polymers[43,44], in particular by treating methylenebis(β-chloropropionamide) with metal sulphides or polysulphides[45].

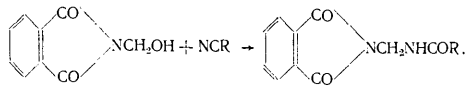
The mechanism of the synthesis of bis-amides has been studied in a number of researches[30,33,46]. It has been suggested that an amide is first formed, which then reacts with the aldehyde. However, the conditions for the preparation of bis-amides from amides and from nitriles are different. Since amides do not react with formaldehyde under the conditions for the synthesis of bis-amides from nitriles, Magat[33] has suggested a mechanism in which carbonium ions take part:

$$CH_2O + H^+ \rightleftarrows HOCH_2^+,$$

$$HOCH_2^+ + RCN \rightleftarrows \overset{-}{R}\overset{+}{C}{=}NCH_2OH \rightleftarrows \underset{OH}{RC{=}NCH_2^+},$$

$$\underset{OH}{RC{=}NCH_2^-} + RCN \rightleftarrows \underset{OH}{RC{=}NCH_2N{=}\overset{+}{C}R} \xrightarrow{H_2O} \underset{O}{RCNHCH_2NHCR}.\underset{O}{}$$

In agreement with this mechanism, *N*-(hydroxymethyl)-phthalimide reacts with certain nitriles in concentrated sulphuric acid to form methylene-bis-amides[47]:



The synthesis of methylene-bis-amides from *N*-(hydroxymethyl)amides and nitriles[48] is essentially the second step of Magat's mechanism:

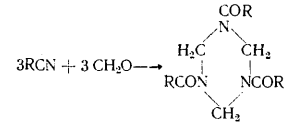
$$RCONHCH_2OH + R'CN \xrightarrow{H_2SO_4} RCONHCH_2NHCOR'.$$

The use of dinitriles in the synthesis of bis-amides has enabled a series of new polyamides to be prepared. The first high-molecular compound of this type (1-*n* polyamides) was obtained by reacting trioxane with azelaic acid dinitrile in sulphuric acid[30]:

$$CH_2O + NC(CH_2)_7CN \xrightarrow[H_2O]{H_2SO_4} \underset{O}{NC(CH_2)_7C}[\underset{O}{NHCH_2NHC(CH_2)_7C}]_n \underset{O}{NHCH_2NHC(CH_2)_7CN}.$$

Adiponitrile and other aliphatic dinitriles[49] and dinitriles obtained by the cyanethylation of glycols[50] have also been used in this reaction. The properties of the 1-*n* polyamides have been studied in detail[49–53]. Treating ω-cyanoundecanoic acid in acid medium with formaldehyde gave a dibasic acid containing the methylene-bis-amide group; a series of polyamides has been prepared by copolymerising the hexamethylenediamine salt of this acid with hexamethylenediamine adipate and ω-aminoundecanoic acid[54].

Heating nitriles to 70°–90° or above with formaldehyde in the presence of catalytic quantities of sulphuric acid gives hexahydro-1,3,5-triacyl-sym.-triazines[29,33,55]:



Aliphatic (saturated and unsaturated) and aromatic nitriles react. The formaldehyde may be used as paraformaldehyde[29,55], trioxane, or α-polyhydroxymethylene[56]. Aldehydes other than formaldehyde do not give this reaction with nitriles. For complete exclusion of water, the reaction may be carried out in the presence of acetic anhydride[55]. 2–20 wt.% of sulphuric acid, based on the initial nitrile, is used. Chlorosulphonic acid[29] is a less effective catalyst than sulphuric acid. An excess of nitrile over the stoichiometric quantity favours the reaction[56].

3. SYNTHESIS OF *N*-SUBSTITUTED AMIDES BY THE RITTER REACTION

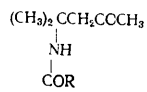
In 1948 Ritter[57] described a new reaction of nitriles with alkenes, with the production of *N*-substituted amides. The addition of isobutylene to acetonitrile and concentrated sulphuric acid in acetic acid at room temperature, with subsequent treatment with a large excess of water, produced *N*-t-butylacetamide in good yield:

$$(CH_3)_2C{=}CH_2 + CH_3CN + H_2O \xrightarrow{H_2SO_4} CH_3CONHC(CH_3)_3.$$

In analogous conversions tertiary and secondary olefines react with hydrocyanic acid, nitriles, and dinitriles of saturated and unsaturated aliphatic acids, and with aromatic nitriles[58–68]. The Ritter reaction has also been carried out with α-hydroxynitriles[63], *N*,*N*-dialkyl-substituted aminonitriles[69,70], β-chloropropionitrile[71], and 1-cyanoformamide[72].

Ritter and his coworkers and others have described the reaction of nitriles with various compounds containing other functional groups in addition to the double bond. *N*-substituted amides have been prepared from certain α,β-unsaturated acids and esters[60], non-conjugated diolefines[73], α-haloolefines[74], and oleic acid[75]. *N*-substituted amides could not be obtained from benzonitrile with methyl acrylate, methacrylate, or crotonate[60]. Formamido-acids have been prepared by the reaction of liquid hydrocyanic acid with oleic and other unsaturated acids[76].

Nitriles can react with certain α,β-unsaturated ketones; in the case of mesityl oxide[77] the reaction proceeds smoothly with the formation of 4-methyl-4-amido-2-pentanones:



It has been shown quite recently[32] that, under the conditions of the Ritter reaction, ketones which undergo the aldol condensation react with nitriles to form β-acylaminoketones.

Secondary and tertiary alcohols[58-60,62] and, less smoothly, their esters[78,79] react similarly to olefines in the Ritter reaction. Corresponding ethers also react with nitriles in the presence of sulphuric acid to form *N*-substituted amides, e.g. benzonitrile and methyl s-butyl ether produce *N*-s-butyl benzamide[80]. Other functional groups may be present in the alcohol; substituted amides have been obtained from β-hydroxyethers[60], α-haloalcohols[74], and 1-phenyl-3-piperidylpropanol[81]. In concentrated acids nitriles react with tertiary alkyl chlorides[82], in the same way as with olefines and alcohols, to form substituted amides.

In addition to 100% sulphuric acid, the catalyst for the Ritter reaction may be 85–95% sulphuric acid[75,76], phosphoric acid[83], benzenesulphonic acid[57], or 90% formic acid[82,84,85]. The reaction also takes place in polyphosphoric acid, although the yields of desired products are lower than with sulphuric acid[86]. Acetic acid, and also dibutyl ether, have been used successfully as solvents[57]. It has been reported[78] that metal salts inhibit the Ritter reaction.

With sulphuric acid as catalyst, the Ritter reaction is usually carried out at 20°–40°, but sometimes, depending on the reactants, a lower temperature (0°)[85], or heating to 55°–65°[69] is recommended. With formic acid as catalyst, the reaction is carried out by boiling the reaction mixture[82,84,85].

In addition to *N*-substituted amides, the reaction of nitriles with olefines may produce simple amides and the corresponding tertiary alcohols[87,88]:

$$RC{\equiv}N + CH_2{=}CR'R'' + 2H_2O \xrightarrow{H_2SO_4} RCONH_2 + R'R''(CH_3)COH.$$

The latter are obtained in good yield if the reaction is carried out in 92% sulphuric acid at 0°–5°. By this method 2,4-dimethylpentan-2-ol, 4-methylheptan-4-ol, and other tertiary alcohols have been obtained from the corresponding olefines. In the absence of nitriles the olefines were polymerised under the reaction conditions.

It is accepted that the first stage in the Ritter reaction is the reaction of the olefine with the mineral acid to form a carbonium ion, which then reacts with the nucleophilic nitrogen atom of the nitrile. This reaction may be schematically represented as follows[48,59,89]:

$$(CH_3)_2C{=}CH_2 + \overset{+}{H} \rightarrow (CH_3)_2\overset{+}{C}{-}CH_3$$

$$CH_3CN + {}^{+}C(CH_3)_3 \rightarrow CH_3\overset{+}{C}{=}NC(CH_3)_3 \xrightarrow{H_2O}$$

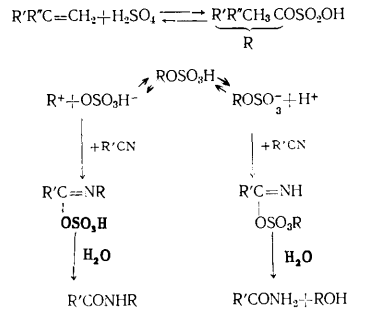
$$\rightarrow CH_3C(OH_2^+){=}NC(CH_3)_3 \xrightarrow{-H^+} CH_3C(OH){=}NC(CH_3)_3 \rightarrow CH_3CONHC(CH_3)_3 .$$

In addition to the carbonium ion, a π-complex of the olefine and mineral acid may also be an intermediate. In this complex the electrophilic properties of the olefine are greater than in the non-complexed compound. Similarly the reaction of tertiary alcohols with nitriles must pass through the formation of a carbonium ion:

$$R\overset{+}{O}H_2 \rightarrow R^+ + H_2O.$$

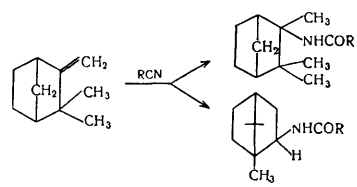
This point of view is confirmed by kinetic studies of the Ritter reaction between acrylonitrile and t-butyl alcohol, in which the t-butyl cation is not formed[15].

When the Ritter reaction is carried out in aqueous sulphuric acid, another mechanism may play an important part, i.e. one involving an alkylsulphuric acid. As shown below, these acids can react with a nitrile in two ways, to form either a substituted or an unsubstituted amide[87]:



It is interesting that when succinonitrile reacts with isobutene under conditions expected to give the *N*,*N*'-disubstituted amide, one nitrile group reacts with the organic cation, and the other with a proton to form an unsubstituted amide group. The *N*-monosubstituted amide $(CH_3)_3CNHCOCH_2CH_2CONH_2$ was obtained[59].

When racemic camphene reacts with hydrocyanic acid in the presence of sulphuric acid, 3-formamidoisocamphane is obtained, instead of the isomeric *N*-formylisobornylamine expected as a result of the Wagner rearrangement. Under the same conditions, *N*-acylisobornylamines have been synthesised from camphene and nitriles[90].



The behaviour of camphene in the Ritter reaction has recently been studied in detail by Kochetkov and coworkers[91], who showed that it condenses with hydrocyanic acid in the presence of one mole of concentrated sulphuric acid at 0° in dibutyl ether, acetic acid, or propionic acid, giving 3-formamidoisocamphane containing 20% *N*-isobornylformamide. The formation of the isobornyl derivative is reduced to a minimum by reducing the reaction temperature to -15° or -20° and carrying out the reaction for 24 h. They also showed[91] that the highly active trichloro- and dichloroacetonitriles react with camphene under the conditions of the Ritter reaction at a reduced temperature similarly to hydrocyanic acid, i.e. without the Wagner rearrangement.

The widest use of the Ritter reaction is found in the synthesis of substituted amides, although it is also of interest as a method of preparation of compounds with an amino group on a tertiary[57,58,68,73] or secondary[75] carbon atom. Yields of compounds with the amino group on a primary carbon atom are low[92]. A number of papers[92-95] have described the synthesis of amines by the reaction of cycloalkanols, secondary aliphatic alcohols, cycloalkyl-substituted aliphatic alcohols, and alicyclic alcohols of spiro structure, with potassium cyanide in the presence of sulphuric acid. In many cases there is intramolecular rearrangement, sometimes leading to an expansion or contraction of the ring.

The reaction of dinitriles with tertiary diolefines has been used to prepare linear polyamides[48,78,82-85]:

$$NC(CH_2)_nCN + R_1CH{=}CR_3C{=}CHR_5 \rightarrow$$
$$\rightarrow NC(CH_2)_nCO[NHCR_2{-}R_3{-}CR_4NHCO(CH_2)_nCO]_n{-}NHCR_2{-}R_3{-}CR_4{=}CHR_5,$$

where R_1, R_2, R_3, R_4, and R_5 are hydrocarbon groups. In addition to aliphatic dinitriles, polyamides have been synthesised from nuclear aromatic (terephthalonitrile), side-chain aromatic (*p*-phenylenediacetonitrile), carbocyclic, heterocyclic, and other dinitriles. Polyamides are also formed by reacting dinitriles with di-secondary alcohols [1,10-dimethyldecan-1,10-diol-1,4-bis-(3-hydroxybutyl)-benzene] and their esters, di-tertiary alcohols (1,1,10,10-tetramethyldecan-1,10-diol), *N*,*N*'-di(hydroxymethyl)-amides, and di-tertiary alkyl chlorides.

Polyamides can similarly be produced from compounds having two different functional groups (hydroxynitriles and chloronitriles in which the hydroxy and chloro groups are tertiary, etc.), for instance from 2-methyl-6-cyanohexan-2-ol. Polymers are formed even when the functional groups are separated by only three carbon atoms; it is known[96] that to prepare polymers by homopolycondensation, the initial monomers must be separated by at least six carbon atoms, or rings are formed.

A patent[97] describes the continuous preparation of *N*-substituted amides from secondary and tertiary alkenes or alcohols at 45°–95° in the presence of sulphuric acid.

In the presence of concentrated acids, certain olefines react with a number of other compounds containing the cyano group as well as with acid nitriles. *N*-t-Pentylbiuret has been prepared from 1-cyanoguanidine and 2-methylbut-2-ene[57]:

$$H_2NCNHCN + (CH_3)_2C{=}CHCH_3 \longrightarrow H_2NCONHCONHC(CH_3)_2C_2H_5.$$
(NH)

The reaction of olefines with cyanogen chloride to form amines has been studied in detail[98] and the following mechanism suggested:

$$>C{=}C< + H^+ \rightleftharpoons >CH{-}\bar{C}<\ ;\quad >CH{-}\overset{+}{C}< + ClC{\equiv}N \longrightarrow >CH{-}C< \xrightarrow{H_2O}$$
(N=CCl)
$$\longrightarrow >CH{-}C< \xrightarrow{+H^+} >CH{-}C< \xrightarrow{H_2O} >CH{-}C< + CO_2 + HCl.$$
(N=C, OH, Cl; HN–C, O, Cl; NH$_2$)

The best catalyst is 96% sulphuric acid, although methanesulphonic, fluorosulphonic, and other acids are also effective. Cyanogen chloride reacts with such olefines as 2-methylbut-1-ene, but-2-ene, and cyclohexene, but not with oct-1-ene or dodec-1-ene.

Thiocyanates react similarly to the nitriles under the conditions of the Ritter reaction[99]; with alcohols and olefines in the presence of sulphuric acid *N*-substituted thiocarbamates are formed:

$$RSCN + R'OH \xrightarrow{H_2SO_4} RSCONHR'.$$

Benzyl thiocyanate and camphene give the corresponding *N*-substituted isobornylamine as a result of the Wagner rearrangement.

4. OTHER SYNTHESES OF *N*-SUBSTITUTED AMIDES

Wieland[100,101] achieved a conversion analogous to the Ritter reaction in 1930 by using hydrogen chloride in the presence of aluminium chloride. Under these conditions *N*-formylcyclohexylamine was synthesised from cyclohexene and hydrocyanic acid. Later[102] cyclohexene was similarly reacted with acetonitrile, phenylacetonitrile, and benzonitrile.

In the presence of aluminium chloride and hydrogen chloride, secondary alkyl halides react with nitriles to form *N*-alkylamides. Apparently $AlCl_3$ removes the halogen from the alkyl halide to form a carbonium ion, this being followed by the formation of a substituted iminochloride, which, when water is added, is converted into the substituted amide[102]:

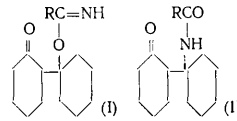
$$RCl + AlCl_3 \longrightarrow R^+ + AlCl_4^-\ ,$$
$$R^+ + R'C{\equiv}N \longrightarrow [R'C{=}NR]^+\ ,$$
$$[R'C{=}NR]^+ + AlCl_4^- \longrightarrow R'C(NR)Cl + AlCl_3\ ;$$
$$R'C(NR)Cl + H_2O \longrightarrow R'C(NR)OH \longrightarrow R'CONHR\ .$$

N-alkylamides are formed comparatively smoothly from cyclohexyl and cyclopentyl chlorides. Under these reaction conditions tertiary alkyl halides produce liquid polymers.

An analogous synthesis of *N*-substituted amides occurs in the reaction of diphenylmethyl bromide with acetonitrile or propionitrile in the presence of silver sulphate[103]. It has been suggested that the primary product is a carbonium ion which then reacts with the nitrile as described above:

$$(C_6H_5)_2CHBr + Ag^+ \rightarrow (C_6H_5)\overset{+}{C}H + AgBr.$$

On adding a mixture of cyclohexanone or its autocondensation product (2-cyclohexylidenecyclohexanone) and acetonitrile (or propionitrile or benzonitrile) to a cooled suspension of anhydrous aluminium chloride in carbon disulphide or dichloroethane and subsequently hydrolysing, a solid made up of two cyclohexanone molecules and one nitrile molecule is obtained; the iminoether structure I[104] was assigned to this compound:



(I)

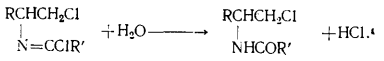
(II),

but later it was suggested[30] and then confirmed[32] that the reaction between cyclohexylidenecyclohexanone and the nitrile takes place by a mechanism analogous to that of the Ritter reaction, the resulting product being 2-(1-acetamidocyclohexyl)cyclohexanone (II).

The preparation of *N*-(2-haloalkyl)amides from nitriles, olefines, and chlorine or bromine, discovered by Cairns and his coworkers[105] is of interest. The first stage of the reaction is the formation of an *N*-(2-chloroalkyl)iminochloride and a 1,2-dichloroalkane:

$$RCH{=}CH_2 + Cl_2 \longrightarrow \overset{+}{R}CHCH_2Cl + Cl^-$$
$$\bar{R}CHCH_2Cl \xrightarrow[Cl^-]{R'CN} \begin{cases} RCHCH_2Cl \\ N{=}C^+R' \end{cases} \xrightarrow{Cl^-} \begin{matrix} RCHCH_2Cl \\ | \\ N{=}CClR' \end{matrix}$$
$$RCHClCH_2Cl$$

If the nitrile does not contain an α-hydrogen atom, the resulting iminochloride can be separated from the dichloroalkane by distillation; if the nitrile contains an α-hydrogen atom, the iminochloride is unstable and undergoes thermal bimolecular condensation with loss of hydrogen chloride. With water the N-(2-chloroalkyl)iminochlorides are converted into the more stable N-(2-chloroalkyl)amides:



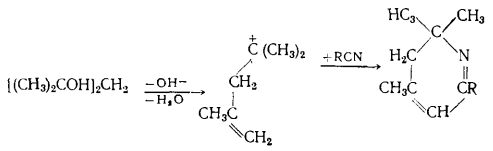
In the case of hydrocyanic acid, the N-(2-chloroalkyl)-formamide is very easily hydrolysed to the 2-chloroalkylamine. Aromatic and aliphatic nitriles and acrylonitrile react in this reaction with ethylene, cyclohexene, oct-1-ene, and styrene.

N-Substituted amides have been prepared by the reaction of nitriles[106-109] and hydrocyanic acid[110] with amines in water at 100°–150° in the presence of acid catalysts. In these studies N-benzylacetamide was obtained from acetonitrile and benzylamine in yields of 1% (in the presence of carbon dioxide), 10% (thiophenol), 20% (hydrochloric acid), 40% (acetic acid), 73% (hydrogen sulphide), and 76% (thioacetamide). Under the same conditions, dinitriles, cyanoamides, and cyanoethers have given N,N'-substituted diamides[111,112]. Unlike other dinitriles, adiponitrile and tetramethylsuccinonitrile do not react; however, there is a patent[113] for the preparation of polyamides from adiponitrile and hexamethylenediamine. In some cases the reaction proceeds without catalysts.

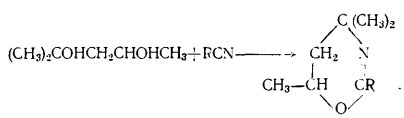
The reaction of hydrocyanic acid with equivalent quantities of an amine and hydrogen sulphide may be used as a general method for the preparation of N-substituted thioformamides[110].

5. PREPARATION OF HETEROCYCLIC COMPOUNDS UNDER THE CONDITIONS OF THE RITTER REACTION

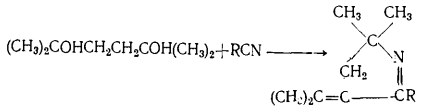
In many cases the Ritter reaction proceeds untypically, with the formation of heterocyclic compounds. The reaction of 2,4-dimethylpentan-2,4-diol with acetonitrile, benzonitrile, or acrylonitrile has produced the corresponding 4,6,6-trimethyl-5,6-dihydropyridines[114]; the reaction may be represented schematically as follows:



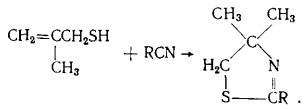
An analogous reaction takes place with 2,4-dimethylhexa-2,4-diene and acetonitrile[88]. The synthesis of dihydro-1,3-oxazines from 2-methylpentan-2,4-diol and nitriles has been described[88,115]:



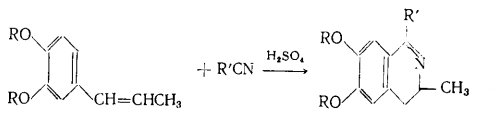
The reaction products of 2,5-dimethylhexan-2,5-diol (or 2,5-dimethylhexa-2,4-diene) with nitriles in concentrated sulphuric acid were 5,5-dimethyl-3-isopropylidene-1-pyrrolines[114]:



The same paper describes the synthesis of 4,4-dimethyl-2-thiazolines from methylallyl mercaptan:

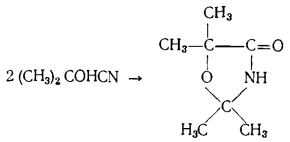


3,4-Dihydroisoquinolines are formed by the reaction (in the presence of concentrated sulphuric acid) of isosafrol, methyleugenol, or methylisoeugenol with veratronitrile, anisonitrile, and certain other nitriles[116,117]:

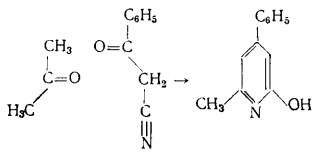


This reaction has been considered as an internal diene synthesis[117].

2,2,5,5-Tetramethyl-4-oxazolidone has been obtained by heating α-hydroxyisobutyronitrile at 85° in the presence of polyphosphoric acid[118]:



Polyphosphoric acid is also a catalyst for the condensation of β-ketonitriles (α-acetyl-α-toluonitrile, benzoylacetonitrile, α-nicotinoylpropionitrile, etc.) with ketones (acetone, phenylacetone, cyclohexanone, etc.) to form substituted 2-pyridones[119], for example:



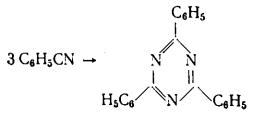
This reaction comprises both condensation and reaction of the nitrile nitrogen atom with an electrophilic carbon atom.

6. PREPARATION OF 1,3,5-TRIAZINES

Even in the early days of organic chemistry it was known[120,121] that nitriles, like simple cyanogen compounds, could polymerise to form triazines. For a long time it was thought[7,122] that triazines could be obtained only from nitriles not containing α-hydrogen atoms; this is not so, for a triazine is also obtained from dichloroacetonitrile[123], but not from trimethylacetonitrile[22].

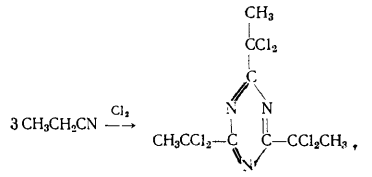
The polymerisation of nitriles is induced by a number of acidic substances, as well as by alkaline[7] and other agents[124]. In the presence of sulphuric acid, alcoholic

hydrogen chloride[34,120,125,126], or chlorosulphonic acid[127,128], benzonitrile has been converted into cyaphenine (2,4,6-triphenyl-1,3,5-triazine):



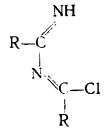
Chlorosulphonic acid has also been successfully used for the conversion of toluonitriles and *p*-chlorobenzonitrile into triazines. It has been reported[129,130] that by treating 3,4-methylenedioxybenzonitrile, 3-methoxy-4-ethoxybenzonitrile, and other substituted nitriles, with chlorosulphonic acid in chloroform, so-called "anthraquinone-diimines" are formed; but Wilson[131] showed that the reaction products are sym.-triazines. The decomposition of phenyl diazonium fluoroborate in aromatic nitriles gives the anilides with the nitrile trimers as by-products[20].

Hydrogen halides are the most frequently used reagents for the polymerisation of nitriles to triazines. In the presence of hydrogen chloride, sym.-triazines have been obtained from trichloroacetonitrile[123,132-134], tribromoacetonitrile[135], trifluoroacetonitrile[136], dichloroacetonitrile[123], benzonitrile[22], and other nitriles. Trichloroacetonitrile is comparatively rapidly polymerised with hydrogen bromide[137]. The polymerisation of trichloroacetonitrile by the combined action of aluminium chloride and hydrogen chloride has been proposed[138]. The formation of 2,4,6-tris-(α,α'-dichloroethyl)-1,3,5-triazine[139,140],

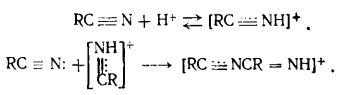


by the chlorination of propionitrile and the formation of 2,4,6-tris(dibromomethyl)-1,3,5-triazine[141] by the reaction of equimolecular quantities of bromine and acetonitrile (in the presence of red phosphorus and calcium carbonate) may be explained by the action of the hydrogen chloride and bromide liberated in these reactions.

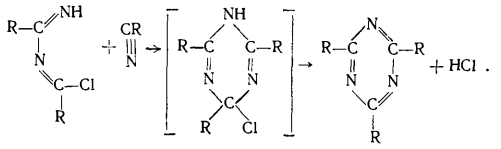
The mechanism of the synthesis of triazines from nitriles in the presence of hydrogen halides has been studied in detail by Grundmann and coworkers[22], who showed that a compound of the nitrile and the hydrogen halide is an intermediate. At normal or elevated temperatures and pressures, depending on the reactivity of the initial nitrile, the intermediate disappears from the reaction mixture and a triazine is formed. In some cases, for example, in the polymerisation of trichloroacetonitrile, the intermediate can be separated as a crystalline material very sensitive to moisture, with a composition corresponding to the combination of hydrogen chloride with two molecules of nitrile; it is apparently a substituted iminochloride:



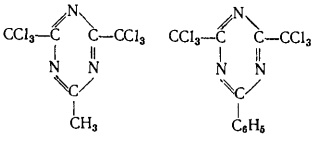
The insolubility of the intermediate in non-polar solvents and its comparatively high decomposition temperature suggest that it has a salt-like structure. The formation of the substituted iminochloride can be considered as a nucleophilic reaction of the nitrile group, with the same nitrile as the electrophilic reagent:



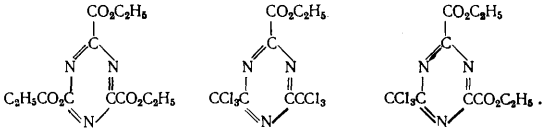
The reaction between the iminochloride and a third nitrile molecule may take place analogously. Grundmann relates the reaction of iminochlorides with nitriles to the diene synthesis:



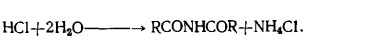
In certain cases the dienophile nitrile is different from the nitrile forming the iminochloride. Trichloroacetonitrile condenses with acetonitrile or benzonitrile, taken in the ratio 2 : 1, to give 2-methyl-4,6-bis(trichloromethyl)-1,3,5-triazine and 2-phenyl-4,6-bis(trichloromethyl)-1,3,5-triazine respectively[22,142]:



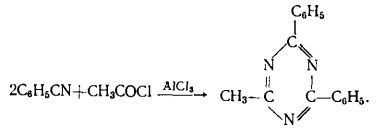
The possibility of mixed condensation for each pair of nitriles is determined by the rates of formation of both possible iminochlorides and their reaction with the nitriles. Sometimes a mixture of triazines is obtained: depending on the reaction conditions, trichloroacetonitrile and ethyl cyanoformate give mixtures of variable composition containing tris(trichloromethyl)triazine, tris(ethoxycarbonyl)-triazine, 2-ethoxycarbonyl-4,6-bis(trichloromethyl)-1,3,5-triazine and 2-trichloromethyl-4,6-bis(ethoxycarbonyl)-1,3,5-triazine:



In the presence of a small quantity of cold water, the substituted iminochlorides which take part in the formation of triazines give secondary amides (imides) in high yield[22,143,144]:

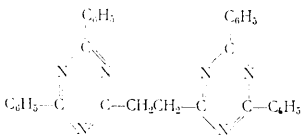


In the presence of aluminium chloride, benzonitrile reacts with aliphatic-acid chlorides to form diphenylalkyltriazines[145,146]:



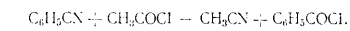
Benzonitrile reacts analogously with dibasic-acid chlorides[147], forming compounds having two rings, e.g.

1,2-ethylenebis(4,6-diphenyl-1,3,5-triazine):



Under these conditions benzonitrile forms dibenzamide with benzoyl chloride[148], but by heating benzonitrile with *m*- or *p*-nitrobenzoyl chloride in the presence of ammonium chloride and aluminium chloride, *m*- and *p*-nitrocyaphenine respectively were obtained[127]. The same method produced the corresponding dinitrocyaphenines from *m*- or *p*-nitrobenzonitrile and benzoyl chloride.

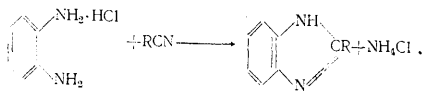
The source of the third nitrogen in the alkyldiaryltriazines was not clear until recently[149]; but in 1956 Meerwein and his coworkers[16] showed that the formation of the triazine is preceded by exchange of functional groups between the nitrile and the acid chloride:



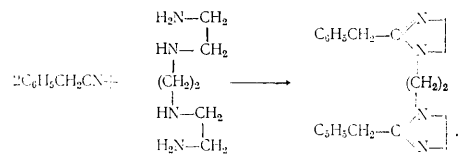
Hence, this triazine synthesis becomes the mixed condensation of two aromatic nitriles and one aliphatic.

7. OTHER SYNTHESES OF HETEROCYCLIC COMPOUNDS

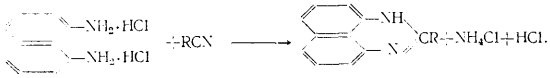
The condensation of *o*-diamines with acid anhydrides, acid chlorides, acids, amides, esters, and substituted amides produces imidazoles. It has been found that an analogous reaction takes place by heating *o*-diamines with nitriles in the presence of hydrogen halides[150,151] or polyphosphoric acid[152]:



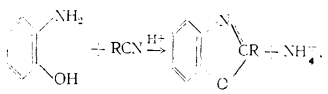
Hydrogen sulphide is a catalyst for the condensation of aliphatic 1,2-diamines with nitriles[153,154]. The reaction of diethylenetriamine and triethylenetetramine with nitriles in the presence of hydrogen sulphide[155] has given aminoethylimidazolines and ethylenebisimidazolines respectively, e.g.



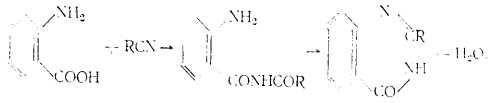
[2-C^{14}]-2-Benzylimidazoline has been synthesised from benzyl[C^{14}]cyanide and ethylenediamine mono-*p*-toluenesulphonate[156]. Certain aromatic diamines produce pyrimidine derivatives[150]:



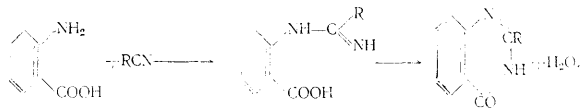
Nitriles react analogously with *o*-aminophenols, the reaction serving as a preparative method for the synthesis of benzoxazoles[150]:



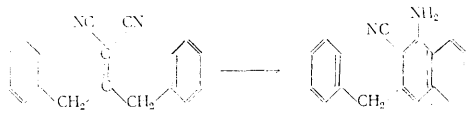
As early as 1898 it was found[157] that on heating to 220°–230° anthranilic acid easily condenses with acetonitrile. The reaction products were later identified, and it was shown that this is a general reaction for aliphatic, nuclear aromatic, and side-chain aromatic nitriles, quinazoline derivatives being formed[158–161]. It was suggested[161] that a secondary amide is the first product:



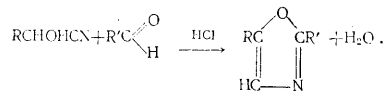
A substituted amidine may also be an intermediate in this synthesis of 2-substituted 4-oxo-3,4-dihydroquinazolines:



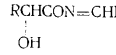
In the presence of polyphosphoric acid, sym.-diphenylisopropylidenemalonitrile undergoes intramolecular condensation to form 3-benzyl-2-cyano-1-naphthylamine[162]:



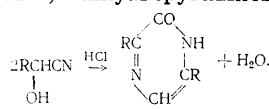
The action of hydrogen chloride on ethereal solutions of aromatic aldehydes and aldehyde cyanhydrins has produced 2,5-disubstituted oxazoles[37,163,164]:



The presence of moisture favours the formation of substituted amides from the same components[37,164]:

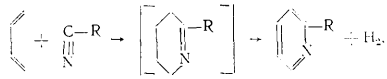


In the absence of aldehydes, α-hydroxynitriles undergo autocondensation in ethereal solutions of hydrogen chloride, to form substituted 3,4-dihydropyrazines[37,165,166]:



The conditions for the above reactions of aldehyde cyanhydrins are identical with those for the synthesis of iminoether hydrochlorides, so that the primary products of these reactions with nitriles, both substituted and unsubstituted with a hydroxy group in the α-position, may be the same. It is also possible that the iminoether hydrochlorides are intermediates in the condensation of aromatic aldehyde cyanhydrins.

Janz and his coworkers[167–179] have developed a vapour-phase synthesis of substituted pyridines from dienes and nitriles:



This is a variation of the diene synthesis. The reaction is carried out at 400° in the presence of mixed aluminium and chromium oxides. If the dienophile component is dicyanogen or trifluoroacetonitrile, the condensation also takes place in the absence of a catalyst. The synthesis of 2-ethylpyridine, from butadiene and propionitrile at 600° in the presence of aluminium oxide, has been described[180].

8. REACTIONS OF NITRILES WITH CARBOXYLIC ACIDS

The reaction of nitriles with carboxylic acids produces secondary amides:

$$RCN + R'COOH \rightarrow RCONHCOR'; \quad (1)$$

but they are not the only reaction products. Often exchange between the nitrile and carboxyl groups occurs:

$$RCN + R'COOH \rightarrow RCOOH + R'CN. \quad (2)$$

In the presence of hydrogen halides, particularly in the cold, the same reagents produce amide hydrohalides and acid anhydrides or chlorides:

$$RCN + 2R'COOH + HCl \rightarrow RCONH_2 \cdot HCl + (R'CO)_2O, \quad (3)$$

$$RCN + R'COOH + 2HCl \rightarrow RCONH_2 \cdot HCl + R'COCl. \quad (4)$$

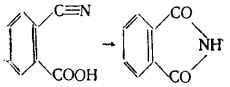
Of reactions (1)–(4), only the first leads to the formation of a new nitrogen–carbon bond, but since the mechanisms of all these reactions have much in common, this review will consider material relating to them all.

The reaction between carboxylic acids and their nitriles was intensively studied at the end of the last and the beginning of the present century, after which practically nothing appeared in the literature for a considerable period. Recently, this reaction has again begun to receive attention.

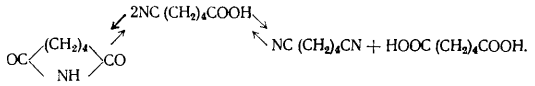
Gautier[181,182] was the first to report on the reaction between aliphatic acids and nitriles. On heating acetonitrile with acetic acid in a sealed tube, he obtained a secondary amide (diacetamide) as product. Similarly, propionitrile and propionic acid give dipropionamide[183]. According to Colby and Dodge[184], a small amount of acetic anhydride may be added to the reaction mixture to increase the yield of secondary amide, in certain cases. They studied the reaction of aliphatic and aromatic nitriles with various acids at 200°–280°, and concluded that: (a) aliphatic nitriles and aliphatic acids form secondary amides according to Eqn. (1); (b) aliphatic nitriles and aromatic acids exchange the acid and nitrile groups according to Eqn. (2); (c) aromatic nitriles and aliphatic acids form mixed secondary amides; and (d) at moderate temperatures aromatic nitriles and aromatic acids form secondary amides; at elevated temperatures reaction (2) is possible.

This classification of the reactions of nitriles with acids is over-simplified. Depending on the reaction conditions, each pair of reactants can form a nitrile and an acid, or a secondary amide, or can undergo both reactions simultaneously. Kŏnig[158] studied the change in the reactivity of nitriles and acids when they are substituted by electronegative substituents, and found that the greater the number of electronegative substituents on α-carbon atoms in the nitrile or acid, the lower the temperature at which the reaction proceeds at a satisfactory rate, and the greater the yield of secondary amide. The favourable influence of electronegative substituents in the nitrile and acid on reaction (1) was also evidenced in the study of the synthesis of diphenylacetamide and α,α'-di(*p*-nitrophenyl)diacetamide[185]. This work also showed that the reaction between the nitrile and the acid is an equilibrium one.

The reaction between nitriles and acids has also been studied when one or both reactants are bifunctional compounds. Treating adipic acid with excess acetonitrile over a short time at 300° produces industrially important adiponitrile[186]. Heating equivalent quantities of succinonitrile and succinic acid gave succinimide in good yield[158]. The reaction temperature can be reduced if the reaction is carried out in the presence of excess mineral acid[187], preferably sulphuric[188]. Succinimide is also formed by heating β-cyanopropionic acid with excess sulphuric acid at 200°–230°. The reaction between the acid and nitrile groups to form secondary amides sometimes takes place even in the cold; thus, on standing, *o*-cyanobenzoic acid is converted to phthalimide[189]:



Nitrile and acid groups in higher cyano-acids also react. On heating, ω-cyanopelargonic acid does not form a cyclic imide, but the functional groups of different molecules react with each other, forming sebacic acid and its dinitrile[190]. In accordance with Carothers' study[96], which showed that the homopolycondensation of compounds with six or seven carbon atoms can take place both by cyclisation and by the formation of linear macromolecules, it has been established that on heating δ-cyanovaleric acid, two reversible reactions occur, producing adipimide and adipic acid and adiponitrile[191]:



The reactions between nitriles and acids, which have often been considered as thermal reactions[158,181,192], are accelerated by catalytic amounts of acids[193,194] and some of their derivatives[193]. The preparation of succinimide from β-cyanopropionic acid, in the presence of $SOCl_2$, PCl_3, $POCl_3$, PCl_5, $AlCl_3$, and CH_3COCl, has been described[188].

The equilibrium nature of the reactions in the system nitrile–acid–secondary amide has been used for the quantitative exchange of nitrile and carboxyl groups in aromatic compounds. Heating a high-boiling nitrile with a low-boiling acid produces an equilibrium mixture containing also the low-boiling nitrile and the high-boiling acid; the equilibrium is displaced by distillation of the low-boiling nitrile. Thus benzonitrile and isophthalic acid are obtained by heating benzoic acid and isophthalonitrile at 237°–287° for 3 h[195]. Similar methods are the basis for the preparation of isophthalic and terephthalic acids[196,197] and their nitriles[198] from the corresponding xylenes. Oxidation of the latter first produces toluic acids; these are oxidised to phthalic acids more slowly than their derivatives, and in particular, their nitriles[195]. To accelerate the process, suggestions have been made to carry it out in accordance with the scheme

$$CH_3C_6H_4CH_3 + 3/2\ O_2 \rightarrow CH_3C_6H_4COOH + H_2O,$$

$$CH_3C_6H_4COOH + NCC_6H_4COOH \rightarrow CH_3C_6H_4CN + HOOCC_6H_4COOH,$$

$$CH_3C_6H_4CN + 3/2\ O_2 \rightarrow HOOCC_6H_4CN + H_2O.$$

To investigate the mechanism of the reaction between nitriles and acids, the reaction between adiponitrile and adipic acid has been studied in the presence of small amounts of additives which accelerate or retard the process[193]. Experiments using equivalent amounts of acids as the catalysts showed that in general the catalytic effect increases with increase of the dissociation constant of the acid catalyst. Acids weaker than adipic do not catalyst the reaction. Solvents having basic properties (dioxan, pyridine, and acetic anhydride) inhibit the reaction between the nitrile and acid to a noticeable extent. On the basis of these results and of studies of the influence of electronegative substituents in the reactants on the course of the reaction[158,185], it has been suggested that the process commences with reaction of the unshared electron pair of the nitrile nitrogen atom with the acid (see the introduction). In the resulting complex the electron density on the carbon atom of the nitrile group decreases (the positive charge increases) as a result of which it reacts with the carboxylic acid to form a protonated isoimide.

$$RCN + HA \rightleftarrows RCN\cdots HA$$

$$RCN\cdots HA + HOOCR' \rightleftarrows \left[\begin{array}{l} RC{=}NH \\ | \\ HO^+{-}C{=}O \\ | \\ R' \end{array}\right]^- \quad (A = \text{anion}).$$

The greater the lability of the proton in the acid, the more positive is the charge on the carbon atom in the nitrile-acid complex, the closer are the properties of this complex to those of the carbonium ion $RC^+{=}NH$, and the more favourable are the conditions for its reaction with the carboxylic acid to form the protonated isoimide molecule. It is known that the interconversion of *N*-acyl and *O*-acyl compounds is accomplished comparatively easily[190-202]; probably this conversion is also possible under the conditions for the reaction of nitriles with acids, leading to the formation of a protonated secondary amide[203-205]. Depending on the reaction conditions and the nature of the radicals R and R', the amide may react with the anion to form a secondary amide, or may rearrange to an ion isomeric with the original cation; this ion easily decomposes into a nitrile and an acid. It has been shown[194] that the formation of the secondary amide,

$$RC(=\overset{+}{N}H)-O-CR' \rightleftarrows RC(=\overset{+}{N}H)-CR' \rightleftarrows RC(-\overset{+}{N}H{=})CR'$$

$$\downarrow A^- \uparrow$$

$$RCNHCR' + HA$$

$$RC(-\overset{+}{N}H{=})CR' \rightleftarrows RC(-\overset{+}{O}-)CR' \xrightleftarrows{A^-} RCOOH + R'CN + HA$$

predominates in the presence of considerable quantities of acid catalysts.

However, a direct reaction of the nucleophilic nitrile molecule with the acid in the presence of an electrophilic agent (scheme *a*) or with an acylcarbonium ion (scheme *b*) cannot be excluded:

(*a*) $R{-}C{\equiv}N: + H^+ \xrightarrow{-H_2O} R{-}\overset{+}{C}{=}N{-}\underset{\underset{O}{\|}}{\overset{R'}{\overset{|}{C}}}{-}OH \xrightarrow[-H^+]{+H_2O} R{-}\underset{\underset{O}{\|}}{C}{-}NH{-}\underset{\underset{O}{\|}}{C}{-}R'$;

(*b*) (*a*) $R'COOH + H^+ \longrightarrow R'CO^+ + H_2O$;

$$R'CO^+ + R{-}C{\equiv}N \longrightarrow R{-}\overset{+}{C}{=}N{-}\underset{\underset{O}{\|}}{C}{-}R' \xrightarrow[-H^+]{+H_2O} RCONHCOR'.$$

The decomposition of the mixed secondary amide to form a new nitrile and a new acid may be represented as follows:

$$R{-}\underset{\underset{O}{\|}}{C}{-}N{=}C{-}R' \xrightarrow{-H_2O} [RCOOH_2]^+ + N{\equiv}C{-}R'$$

$$[RCOOH_2]^+ \xrightarrow{H^+} RCOOH + H^+$$

Sometimes, in addition to the formation of a secondary amide and the exchange of the nitrile and acid groups, heating mixtures of nitriles and acids also produces small quantities of the amides and anhydrides or acid diborides [reactions (3) and (4)][194]. A stoichiometric excess of acid over nitrile favours this reaction.

If the nitriles and acids are reacted at low temperatures in the presence of a large amount of hydrogen chloride, this reaction is the main one. Colson[206,207] was the first to show that in the presence of acetic acid and hydrogen chloride, acetonitrile and propionitrile are converted at 0° into the corresponding amides, the acetic acid forming acetyl chloride. The same products were obtained when the acetic acid was replaced by acetic anhydride. Krieble[208] suggested carrying out this reaction in an organic solvent, and used it for the synthesis of anhydrides of chloro-substituted acetic acids.

Colson[206] assumed that the first stage in this process is the reaction of the acetic acid with the hydrogen chloride to form acetyl chloride and water, which then adds on to the nitrile. Closer to modern views on the mechanism of such reactions is the suggestion[208] that initially the nitrile and hydrogen chloride form an iminochloride, which produces a secondary amide with the carboxylic acid. A second carboxylic acid molecule is acylated by the secondary amide, with the formation of the final reaction products:

$$RCN \xrightarrow{HCl} RC(=NH)Cl \xrightarrow{R'COOH} \underset{RCNHCR'}{\overset{O\ O}{\|\ \|}} \xrightarrow{R'COOH} RCONH_2\cdot HCl + (R'CO)_2O.$$

It has recently been shown[209] that in the presence of large amounts of inert solvents, the nitrile and hydrogen chloride first form a chloroimonium chloride, which reacts with the carboxylic acid to give a protonated isoimide, which is a more effective acylating agent than a secondary amide[205]:

$$RC{\equiv}N + 2HCl \rightleftarrows \left[RC(=NH_2)Cl\right]^+ Cl^- \xrightleftarrows{R'COOH} \left[\underset{NH_2O}{\overset{RCOCR'}{\|\ \|}}\right]^+ Cl^- \xrightarrow{R'COOH}$$

$$\rightarrow \left[RC(=NH_2)OH\right]^+ Cl^- + (R'CO)_2O.$$

The acid chloride may be formed as a result of a secondary reaction between the anhydride and the hydrogen halide[207,210], and possibly also by the direct reaction of the isoimide with hydrogen chloride.

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REVERSIBLE PHOTOCHEMICAL REDUCTION OF CHLOROPHYLL AND ITS ANALOGUES AND DERIVATIVES

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INTRODUCTION

One method of obtaining knowledge about the photochemical stage of photosynthesis is to study the changes undergone by plant pigments on exposure to light. In 1948 we succeeded in detecting the ability of chlorophyll and its analogues to undergo reversible photochemical reduction[1]. This reaction is accompanied by the formation of active photoproducts, which "store" the energy of the light quanta, reacting reversibly after the termination of the exposure to regenerate the original pigment molecule. Further research showed that reversible photoreduction forms the basis of the photosensitising action of chlorophyll in solution, and can be used to explain the mechanism of several photobiological processes. During the past decade much work in the USSR and abroad has been concerned with the photoreduction of chlorophyll and its analogues and derivatives, and it is timely to review this work now. Brief summaries have been given in previous papers by the present author[2].

The Laboratory of Photobiochemistry of the Institute of Biochemistry of the Academy of Sciences of the USSR has carried out a comparative study of the properties of chlorophyll and its analogues and derivatives, which has enabled us to determine the significance of individual molecular groupings in the pigments and of the nature of the central metal atom in the development of photochemical properties. Investigations have been carried out on pigments isolated from various organisms and purified by chromatography, and also on pigments in the form of natural proteins directly in biological structures (in suspensions of granules and chloroplasts) and the leaves of plants.

Studies have been made on chlorophylls *a* and *b* of green leaves, bacteriochlorophyll of photosynthesising bacteria, protochlorophyll of etiolated leaves and the seed capsules of the Cucurbitaceae, the corresponding phaeophytins, various

porphyrins, phycobilins, and on synthetic analogues of these pigments, the phthalocyanines. In the course of this work methods for the separation and chromatographic purification of these plant pigments were worked out and applied.

All the pigments studied have characteristic absorption and fluorescence spectra, which vary not only with chemical changes in the pigments, but also with change in their molecular condition, e.g. aggregation to form colloidal particles, formation of coordination compounds, etc. The investigations reported below were therefore based on spectrophotometric measurements made photoelectrically during the course of reaction. Spectrophotometry in vacuum tubes adapted for measurements using Beckman and SF-4 instruments was extensively employed in the work. The reaction was also studied in several cases by making measurements of fluorescence spectra, the photoelectric potential of an inert electrode, and the photoconductivity of the reaction mixture. The formation of free radicals during the reaction was measured by methods based on the initiation of photopolymerisation and on electron paramagnetic resonance.

The following methods were employed to study the active reaction intermediates and to disentangle the separate stages in the reaction: (1) use of media in which the intermediate reaction products are stabilised; organic bases were found to have such an effect; (2) use of low temperatures, which allowed the photochemical stage of electron transfer to be isolated from the subsequent dark stages of the reaction; and (3) use of deuterated hydrogen donors which, together with the experiments at low temperatures, enabled the proton-transfer stage to be studied.

All these methods were employed in combination with measurements which enabled the formation of photoproducts to be followed directly during illumination of the reaction system and the products which "survived" the period of exposure to be traced.

I. REVERSIBLE PHOTOREDUCTION

1. Spectrophotometric Measurements

Chlorophyll. Brief exposure to red light of pyridine solutions of chlorophyll containing a reducing agent (ascorbic acid or phenylhydrazine) without access of air leads to the formation of a "red" photoreduction product having an absorption maximum at 520–525 mμ. When the light is switched off, the reverse reaction occurs, with regeneration of the chlorophyll and restoration of the green colour of the solution; this happens more rapidly when oxidising agents, atmospheric oxygen, etc., are introduced[1,2].

Partial conversion to phaeophytin was observed as a side reaction, especially in the presence of excess of ascorbic acid and with longer periods of illumination. The reversibility of the reaction was the more complete witn chlorophyll *a*; with chlorophyll *b* reduction in pyridine also gave products which could not be reconverted[3].

Reaction could be observed also in alcoholic solutions containing organic bases — pyridine, nicotine, phenylhydrazine, hexamethylenetetramine — and in pyridine in the presence of up to ~ 50% of water[3,4].

Continuing these investigations, Evstigneev and Gavrilova[5] showed that in toluene solution chlorophyll is photoreduced by phenylhydrazine. Under these conditions it was possible to photoreduce chlorophyll *b* with good reversibility. When the temperature was lowered to -40°, the formation of the "red" photoreduced form of chlorophyll was extremely slow.

Holt and Rabinowitch[6], repeating our experiments, noted that the photoreduction and its reversal could be carried out over and over again with the formation of an ever increasing amount of irreversibly changed chlorophyll. Linshitz and Weissman[7] observed the formation of a "red" photoreduced form of chlorophyll in phenylhydrazine. Lynch and French[8] repeated the photoreduction of chlorophyll in pyridine, and noted that reaction can be observed on adding 50% of pyridine to an aqueous suspension of chloroplasts. Rackow and Konig[9], in a study of the photoreduction of chlorophyll, showed that when the cyclopentanone ring of the chlorophyll molecule was broken, they were unable to observe the reaction, which in their opinion shows that this group must be present in the molecule for the reaction to occur. This conclusion is evidently unjustified, since several other analogues and derivatives of chlorophyll which contain no cyclopentanone ring (porphyrins, magnesium phthalocyanine) are fully capable of photoreduction.

Bannister[10], in his thesis on the reversible photoreduction of chlorophyll, concluded that the reaction takes place only when alcohol or water is introduced into the pyridine, which favours the formation of the ascorbate ion the active electron-donor. The quantum efficiency for the formation of the "red" reduced form of chlorophyll reaches 0.05 with 40% of water in the pyridine; formation of phaeophytin was also observed during the photoreaction. In ethereal solution, free from oxygen, chlorophyll is photoreduced by phenylhydrazine to a form having absorption maxima at 410 and 520 mμ. In agreement with the work carried out in our laboratory, Bannister concludes that it is not a singlet but a triplet excited state of chlorophyll which takes part in the reaction.

Phaeophytin. We have observed the reversible photoreduction of phaeophytin with the formation of a "red" form having a similar spectrum to the corresponding form of chlorophyll[3].

Detailed comparative studies of chlorophyll and phaeophytin were made by Evstigneev and Gavrilova, who observed a more rapid reduction of phaeophytin[11]. They found that at -40° in pyridine solution phaeophytin forms a brown intermediate photoproduct, which passes into the red photoreduced form on heating[12]. This "primary" reduced form of phaeophytin and other pigments has been investigated in detail by Evstigneev[13].

Ethyl chlorophyllide. This behaves like chlorophyll, giving a "red" reduced form. Holt[14] noted the reversible photoreduction of the chlorophyllide in the presence of Versene (tetrasodium ethylene diaminetetraacetate).

Protochlorophyll and its derivatives. On photoreduction with ascorbic acid, protochlorophyll forms a brown photoproduct, with an absorption maximum at 470 mμ, which is reversibly reoxidised to form the green protochlorophyll[15]. It was not possible to observe the formation of chlorophyll, although prolonged illumination leads to the formation of a small amount of a product having an absorption maximum at 675 mμ. Protophaeophytin is also capable of reversible photoreduction. Destruction of the cyclopentanone ring of these compounds by means of piperidine or alcoholic alkali leads to the formation of porphins, which are photoreduced like other porphyrins

(see below). Evstigneev and Gavrilova measured at -40° the absorption spectra of the primary photoreduced form of protophaeophytin which has analogous properties to those of the primary photoreduced form of phaeophytin[16].

Bacteriochlorophyll and bacteriophaeophytin. The photoreduction of bacteriochlorophyll by ascorbic acid in pyridine results in the formation of photoproducts which possess no characteristic absorption spectrum in the visible region[17]. Reaction is more complete, and more reversible, in strongly basic media, i.e. in the presence of piperidine, ammonia, or phenylhydrazine as reducing agents. With sodium sulphide the reaction is readily reversible in air, and a green photoreduction product with a maximum at 660 mμ is formed.

Bacteriophaeophytin under these conditions forms a stable green photoreduction product[17].

Bacterioviridin. A study of the properties of the pigment of green sulphur bacteria, which are similar to those of chlorophyll, has shown that this pigment forms a "red" photoreduced form like the photoreduction product of chlorophyll *a*. The phaeophytin obtained from bacterioviridin also has similar properties to phaeophytin *a*, forming primary and secondary photoreduced forms. Bacterioviridin differs from chlorophyll in its greater rate of photooxidation in solution; in this it approaches bacteriochlorophyll, breaking down extremely rapidly on illumination.

Porphyrins. Protoporphyrin, haematoporphyrin, the porphyrin of photosynthesising bacteria, and the porphyrin obtained from protochlorophyll proved to be similar in behaviour; differences were observed only in the rates of the forward and reverse reactions[19-21].

The photoreduction of these compounds has been studied in organic solvents and in acid and alkaline aqueous solutions. In the bases (piperidine and pyridine) reaction with ascorbic acid usually leads to the formation of a green photoproduct, having an absorption maximum at 640–660 mμ, which is reversibly reconverted into a porphyrin in the presence of air. In water containing 10% of pyridine a photoproduct with maximum absorption at 740–750 mμ is formed[19]. The two compounds are linked by an acid–base equilibrium, passing from one into the other with change in the basicity of the medium[20]. These products evidently differ in the degree of dissociation of the carboxyl groups of the porphyrin.

In acid aqueous solutions the absorption spectrum of the porphyrins is markedly changed by the addition of protons to the nitrogen atoms of the pyrrole nuclei; an intermediate photoreduced product having maximum absorption at 520 mμ is formed[21] (see Fig. 2).

At -40° formation of a "primary" form of haematoporphyrin with a maximum at 450 mμ was observed; on heating this underwent partial conversion into a "green" photoreduced form with an absorption maximum at 650 mμ[16].

Metal complexes of chlorophyll and its analogues. We have been unable to photoreduce the copper complexes of phaeophytin, but the fluorescent zinc complex was capable of photoreduction in the experiments of Vostrilova and Dulova[22]. Rackow and Konig[9] pointed out the facile reversibility of the photoreduction of this compound.

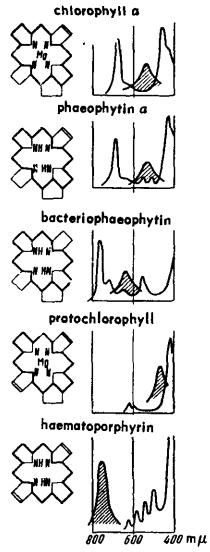


Fig. 1. Changes in the absorption spectra of chlorophyll and its analogues on photoreduction with ascorbic acid in pyridine[2] (skeletal structure of pigment molecules shown); the curves show the shape of the absorption spectrum of the pigment before reaction and after the reverse reaction; the absorption spectra of the intermediate photoreduced forms are shaded.

Dain and his collaborators[23,24] established and made a detailed investigation of the photoreduction of iron complexes of chlorophyll; they assumed that the reaction involves electron transfer with a complex of the iron–chlorophyll with hydroxide ions, water molecules, and

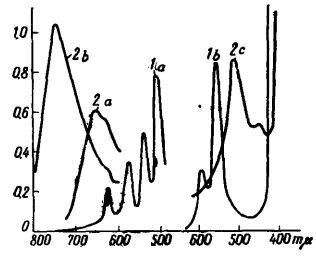


Fig. 2. Absorption spectra of photoreduced forms of haematoporphyrin in basic and acidic media[20-21]: 1) absorption spectrum of porphyrin before photoreduction and after the reverse reaction in the dark: *a*) in a pyridine–ethanol mixture; *b*) in *N* H_2SO_4; 2) after photoreduction with ascorbic acid: *a*) in pyridine; *b*) in a pyridine–ethanol mixture; *c*) in *N* H_2SO_4.

metal ions from the reducing agent. Dain and Ashkinazi [23,24] supposed that in the excited state the electronic system of these pigments is unstable, leading to subsequent (after absorption of light) electron transfer within the complex from the organic skeleton of the molecule to the central iron atom, which thus undergoes photoreduction. The resulting charge deficiency is made up by oxidation of the solvent. Since these electron transfers, following one upon the other, occur immediately after the actual absorption of light, the life of the excited state is considerably shortened. This is shown, in the opinion of these workers, by a slight broadening of the absorption bands, and the disappearance of fluorescence and the vibrational structure.

We have observed an extremely slow photoreduction of cytochrome *c* under the influence of visible light in anaerobic conditions, and the photooxidation of its reduced form in the presence of air [25,26].

Phthalocyanines. In the irradiation of a pyridine solution of magnesium-phthalocyanine containing ascorbic acid, the formation of irreversibly reduced products was accompanied by a photoreduction stage which could be rapidly reversed in the dark [27].

On carrying out the reaction at a low temperature, Evstigneev and Gavrilova observed a rapid formation of the "red" photoreduced form with a maximum at 550 mμ, which on admission of air was instantly converted back to the original phthalocyanine [28]. As in the case of chlorophyll, the spectrum of the "primary" photoreduced form of this compound could not be obtained. Copper-phthalocyanine does not undergo a reaction of this type.

Carotenoids. Attempts have been made in our laboratory to detect the photoreduction of β-carotene, xanthophyll, and the carotenoids of photosynthesising bacteria in various media with different reducing agents, but under no conditions was it possible to observe the formation of reversibly reduced products of these compounds [29]

Phycobilins. The phycoerythrin of red algae and phycocyan do not undergo this reaction nor have any photosensitising action [30]; attempts have been made to photoreduce erythrobilin, obtained by the acid hydrolysis of phycoerythrin, but this compound also proved unable to enter into a photoreaction.

2. Pigment Structure and Capacity for Photoreduction

On the basis of the above results we came to the conclusion that photoreduction can be observed with all derivatives and analogues of chlorophyll which possess a chlorin, bacteriochlorin, or porphyrin structure with a central atom of hydrogen, magnesium, or zinc.

The spectroscopic properties and the reactivities of the reduced forms of the various pigments are different in different media. Magnesium complexes usually form more active (more rapidly reconverted) reduced forms than do phaeophytins, containing no magnesium.

Comparison of the reactivity with the structure of the various pigments shows that the main criterion determining the reversible photoreduction of a pigment is the presence in its molecule of a cyclic system of conjugated double bonds linking the four pyrrole rings.

3. Comparison of the Properties of Intermediate Forms Produced by Photoreduction and by "Dark" Reduction with Zinc

Timiryazev was the first to discover the ability of chlorophyll to be reduced by metallic zinc and its subsequent regeneration by the action of air on the reduced compounds [31].

Kuhn and Winterstein demonstrated the identity of chlorophyll *a* before reduction with zinc and after reoxidation [32]. Rothemund, Albers, and Knorr [33] showed that the spectra of the pigment after regeneration and of the original chlorophyll are not identical.

In our laboratory [34] a study has been made of the reduction of chlorophyll and its analogues in pyridine solution with metallic zinc in the presence of acetic acid; under these conditions regeneration is followed by replacement of magnesium by zinc with formation of a zinc complex of the chlorophyll. The intermediate products include a compound having the spectrum of the "red" photoreduced form of chlorophyll. Evstigneev and Gavrilova [35] studied the effect of the amount of acid present on the zinc reduction, and found that with a minimum quantity of acid it is possible to obtain a reduction product of chlorophyll whose spectrum is identical with that of the "red" photoreduced form, from which chlorophyll, and not its zinc complex, is regenerated.

When a pyridine solution of chlorophyll is reduced with zinc amalgam in a vacuum, products having a different absorption spectrum from that of the red form are formed. Possibly, under these conditions partial formation occurs of products, of a one-electron reduction, corresponding to the primary photoreduced form of chlorophyll, whose spectrum has not yet been determined; on exposure to oxygen, the reverse reaction occurs instantaneously with formation of chlorophyll. Reduction of haematoporphyrin under these conditions leads to the formation of a product spectroscopically identical with the "primary" photoreduced form.

Thus it is possible, by varying the conditions of reduction of chlorophyll with zinc, to obtain intermediate compounds which are identical with photoreduction products.

4. Changes in Fluorescence during Photoreduction

All the porphyrin pigments studied possess a characteristic fluorescence, usually red in colour, only bacteriochlorophyll having a fluorescence maximum in the near infra-red region (780 mμ).

At the start of the investigation we observed that photoreduction is accompanied by a reversible diminution in the red fluorescence of chlorophyll and the appearance of the orange luminescence of the photoreduced form at 600–630 mμ. Evstigneev [5] observed, on cooling photoreduced chlorophyll to the temperature of liquid nitrogen, the appearance of a green fluorescence with maxima (in toluene solution) at 525–520 and 550–570 mμ. Gachkovskii [36] described the appearance of a series of fluorescence maxima, including an intense maximum at 730 mμ, during the photoreduction of chlorophyll and phaeophytin.

Krasnovskii and Erokhin [37] have undertaken systematic studies on the fluorescence spectra of pigments during their photoreduction with ascorbic acid in pyridine. With all the pigments investigated — chlorophyll *a* and *b*, protochlorophyll, bacterioviridin, and the corresponding phaeophytins

and porphyrins — fluorescence of the photoreduced forms was observed. Only in the case of the primary photoreduced forms of phaeophytins were well defined fluorescence maxima not found at low temperatures. We were also unable to observe the fluorescence maximum at 730 mμ of the photoreduced form of chlorophyll and phaeophytin described by Gachkovskii[36]. It is evident that in this work the fluorescence was recorded together with incident light scattered by the frozen material. A group of mercury lines near 733 mμ was used and was probably transmitted by the combination of light filters.

5. Change in Redox Potential E_0 during the Photoreaction

Krasnovskii and Brin[38] used a redox-indicator method to estimate the shift in E_0 for the system after reaction. The photoreaction of chlorophyll with ascorbic acid was carried out in a vacuum tube having a side outlet, after which solutions of compounds having different values of E_0 were run into the photoreduction products in the dark, and the rate of the reverse reaction was observed spectrophotometrically.

Before exposure, the chlorophyll–ascorbic acid system in pyridine can reduce compounds having E_0 about 0.05 V (methylene blue), but after exposure reduction of compounds with E_0 about -0.35 V (safranine T, pyridine nucleotides) was observed. These results were confirmed by measurements of the potential of an inert electrode in the reaction system. We observed a sharp change in the potential of such electrode on illuminating the chlorophyll–ascorbic acid system, as in the experiments of Rabinowitch[39] on the thionine–iron ions system.

Evstigneev and Gavrilova made a detailed study of the variation of the photoelectric potential of a platinum electrode on illumination of the reaction solution[40]. It had been shown in special experiments that the photopotential is determined not by the illumination of the electrode but by the formation of photoproducts in the bulk of the solution. Lowering the temperature was observed to increase the value of E_0 owing to the decrease in the rate of the reverse reactions and the increase in the steady-state concentration of the photoproduct. The change was observed at -40° (i.e. under conditions such that no formation of the "red" form of chlorophyll occurred). These observations led to the conclusion that the potential is determined by the formation of the primary, readily reconvertible "electrode-active" reduced form of the pigments, studied in detail by Evstigneev[13]. The intermediate formation of the "primary" reduced form was also supported by Bannister's work[10] on the quantum efficiency of the reaction as a function of the concentration of reducing agent. On illumination of solutions of chlorophyll and its analogues containing ascorbic acid the value of E_0 reached -0.35 V, in agreement with the experiments in which redox indicators[38] were used. Thus the "electrode-active" form and the "red" reduced form have similar values of E_0.

Hendrich[41] observed a change in the photoelectric potential on illumination of the chlorophyll–ascorbic acid system, and studied the effect of a series of inorganic ions on this process. He found that Cu^{2+} and Ni^{2+} ions, which can combine with ascorbic acid, prevent the development of a photoelectric potential.

On illuminating the chlorophyll–phenylhydrazine system in a vacuum, Evstigneev and Gavrilova observed an increase in electrical conductivity[42]; when the light was switched off, the conductivity returned to its previous value, which confirms the formation of ionic photoproducts. Comparison of the kinetics of the photoconductance and of the development of the photopotential at different temperatures indicates that it is the "electrode-active" products which are responsible for the photoconductivity. Thus at -40° the photoconductivity and the photopotential remain after the light has been switched off, whereas at +20° the effects are rapidly reversed in the dark.

The potential of a platinum electrode in the chlorophyll–ascorbic acid system in pyridine becomes 0.3–0.35 V more negative after illumination, indicating the formation of electrode-active products (the photoreduced form of the pigments), which give up their electron to the electrode in accordance with the following scheme for the primary photoprocess:

$$X + AH_2 \rightleftharpoons \cdot X^- + \cdot AH_2^+; \quad AH_2^+ \rightarrow \cdot AH + H^+;$$

further dissociation is possible in the presence of strong bases:

$$\cdot AH \rightarrow A^- + H^+.$$

The question arises as to why the negatively charged platinum electrode takes up the charge of the reduced form of the pigment, but does not give up an electron to the oxidised form of the hydrogen-donor.

Factors which play a part here are evidently the preferential adsorption of photoproducts of a given character on the platinum and the kinetics of the secondary changes undergone by the photoproducts. If, for example, the rate of dismutation of one of the pair of semiquinones ($\cdot X^-$ or $\cdot AH_2^+$) is greater than that of the other, the steady-state concentration of the latter compound will be greater than would appear from the electrode potential. In addition, the oxidised product (monodehydroascorbic acid) ·AH is probably able to act as a reducing agent, giving up an electron to the electrode with the formation of dehydroascorbic acid. It is thus possible that both photoproducts formed during the reaction will tend to give up an electron to the electrode. It is therefore desirable to investigate the electrode activity not only of the primary reduced form of the pigments but also of the "semi-oxidised" compound which is formed.

In this connection it is useful to compare what happens with a reducing agent which is chemically quite different in character, namely ferrous ions. Krasnovskii and Umrikhina[21] have studied the photopotential of a platinum electrode in aqueous acid solutions of a porphyrin–ascorbic acid system; here the photopotential became more negative, just as in the chlorophyll–ascorbate system in pyridine. However, with ferrous oxalate as electron-donor, the photopotential became more positive, evidently because the ferric ions formed by the elementary photoprocess

$$X + Fe^{2+} \rightleftharpoons \cdot X^- + Fe^{3+}$$

are more electrode-active. The kinetics of the photopotential variation of an electrode in these systems require more detailed study.

6. Reductant Molecules (Electron-Donors) which React with Chlorophyll and its Analogues

The reaction was observed in its purest form, yielding long-lived products in pyridine, using ascorbic acid and other dienols, phenylhydrazine, hydrogen sulphide, or cysteine[1-3]. To investigate the readily reversible "latent"

formation of primary photoproducts, it was necessary to use methods enabling such formation to be observed during the period of illumination. Sensitive methods were: measurement of the photopotential, sensitised photopolymerisation, and sensitised reduction of irreversibly reducible electron-acceptors.

A change in E_0 towards more negative values was produced by the reaction with chlorophyll of quinol, catechol, thiosinamine, and several other compounds[13]. Oster and Holt[43] used ethylenediaminetetraacetic acid in reactions of this type. The activity of ferrous compounds was shown by the polymerisation method[44,45]. The sensitised oxidation of cytochrome in the presence of chlorophyll, which we have observed[25,26], indicates the possibility of a reversible process here also. It appears from the experiments of Rackow and Konig[9] that haemochromogens could be used as electron-donors. Thus, an excited chlorophyll molecule can acquire an electron from systems with values of E_0 between -0.3 and +0.3 V.

It is probable that chlorophyll could react with cytochrome *b* detected in chloroplasts[46], for which the value of E_0 is close to that for ascorbic acid. Up till now it has remained obscure whether an excited pigment molecule can acquire an electron from a water molecule.

Use of deuterated donors. The use of deuterated ascorbic acid slows down the photoreduction of chlorophyll and the production of the "red" form[47]; the reverse dark reaction also takes place more slowly. Hill's reaction is retarded by increasing the quantity of D_2O in the water[47].

The D_2O, while retarding formation of the "red" form of phaeophytin, does not affect the rate of formation of the "primary" photoreduced form[48]; at low temperatures the rate of formation of the primary form of phaeophytin is the same whether the ascorbic acid used is deuterated or not[48]. These observations confirm the occurrence of electron transfer in the formation of the "primary" form and the participation of a proton in the formation of the more stable "red" form.

Reaction with solvent. Porret and Rabinowitch[49] were the first to observe the reversible decolorisation of chlorophyll in methanol. Livingston[50-52] studied the reversible spectral changes, occurring in chlorophyll solutions, by flash photolysis and found an increase in absorption at 525 mμ, corresponding to the maximum for the photoreduced form of chlorophyll. Linshitz and Rennert[53] detected reversible changes in the absorption spectrum of chlorophyll on illuminating it in vitreous media at low temperatures. Linshitz and Abrahamson[54], using the technique of flash photolysis with chlorophyll solutions in pyridine, noted a reversible lowering of the absorption maximum of chlorophyll in the red region of the spectrum and the appearance of a maximum in the green region at 525 mμ, together with a slight increase in absorption at 700 mμ. They noted that the life of the product absorbing at 525 mμ is longer in pyridine than in other solvents, and the reversibility of the process is better than in purified methanol.

Terenin and his collaborators[55] observed by means of a flash technique a reversible fall in the absorption maximum in solutions of magnesium-phthalocyanine, and the appearance of new maxima in haematoporphyrin[56].

In experiments of this type the solution is subjected to the action of an extremely powerful flash of light, lasting for about 10^{-5} sec, produced in a discharge tube by the discharge from a bank of condensers (50 joules); a "recording" light flash from another discharge tube is passed through the solution $10^{-4}-10^{-5}$ sec after the activating flash.

We have already suggested[57,58] that the effects observed in these experiments can be explained by the reversible photoreduction of chlorophyll, in which solvent molecules act as electron (hydrogen) donors. Actually, oxygen inhibited reversible effects in Livingston's experiments in conformity with the rapid reaction of oxidising agents with the photoreduced form of chlorophyll.

The fact that, in the flash photolysis experiments, formation of photoreduced forms of the pigment is mainly observed is supported, in our opinion, by comparatively recent experiments of Livingston and Fujimori[59]. They studied the effect of various compounds on the half-life $\tau_{1/2}$ of the metastable excited state of chlorophyll, and found that oxidant molecules shorten $\tau_{1/2}$, whereas reducing agents (ascorbic acid) have no effect on the value of $\tau_{1/2}$.

These results are readily understood on the assumption that a photoreduced form of chlorophyll is produced by the light flashes; clearly, this form will not react with a reducing agent (ascorbic acid) but does react with an oxidising agent (quinone). The effect of carotene in these experiments agrees with the effect of this compound on the photoreduction of chlorophyll observed in our own experiments[29,60].

The spectrum of the "triplet" state in the papers of Livingston and Linshitz is similar to that of the "primary" photoreduced form of phaeophytin observed by Evstigneev, and it contains also an absorption region corresponding to the "red" form of chlorophyll. In these experiments the main effect is evidently the absorption of an electron by an excited pigment molecule, whereas any formation of a shorter-lived metastable state is superimposed on the main effect and is difficult to distinguish with the recording technique employed (see also Terenin[56]).

7. Effect of the Acid–Base Properties of the Medium

Formation of relatively stable photoreduced forms of chlorophyll can be clearly observed in pyridine. We have already put forward the hypothesis that this stability is associated with acid–base equilibria, under which the proton is situated "between" the pigment molecule which has absorbed an electron and a molecule of the medium, a base:

$$\cdot X^- \,..\, H^+ \,..\, N\!<$$

The formation of these relatively stable compounds is possible only when the proton affinities of the pigment molecule and of the medium (the base) have certain values. The optimum basic strength of the medium for the formation of stable reduced forms differs with different pigments. It was to be expected that in a more basic medium than pyridine, formation of negative radical-ions $\cdot X^-$, readily undergoing the reverse reaction, would predominate. In more "acidic" media the formation of radicals $\cdot XH$ could be expected with the addition of a single proton, and of positively charged radical-ions $\cdot XH_2^+$ with the addition of two protons.

In fact, if a few drops of a strong base, piperidine or ammonia, are added to a pyridine solution of the "red" form, the reverse reaction occurs rapidly (owing to ionisation of the reduced form)[20]; in conformity with this, piperidine or ammonia, added to a pyridine solution of chlorophyll, hinder the formation of the "red" form during the photoreaction. These experiments must be carried

out quickly and preferably at low temperatures, since even 1% of piperidine in pyridine leads to a gradual breakdown of the cyclopentane ring of the chlorophyll molecule. If the reaction is carried out in pyridine which has been carefully dried with calcium hydride, formation of the "red" form takes place far more slowly than in ordinary reactive, moist pyridine, which is explained by the presence of insufficient "hydrogen ions" in the dry pyridine for the formation of the "red" form.

In the case of haematoporphyrin, a reduced form with an absorption maximum at 650 mμ is formed in strongly basic media (piperidine), but in less basic media (alcohol–pyridine mixtures) one with a maximum at 740 mμ is produced. By varying the basic strength of the medium, it is possible to change repeatedly and reversibly the position of the absorption maximum of the reduced forms[20].

Thus the conversion of the "650" into the "745" form is governed not by different redox levels, as was assumed earlier[19], but by acid–base equilibria. An optimum acidity is observed for the formation of the reduced forms of different pigments with zinc according to the method of Timiryazev[35].

Thus the spectral properties and reactivities of photoreduced forms of the pigments vary within wide limits depending on the basic strength of the solvent. More detailed study is required of the effect of the basic strength of the medium on the properties and behaviour of the electron-donor molecules which are "semi-oxidised" during the reaction; it must be assumed that monodehydroascorbic acid is also more stable in basic media, where it occurs in the form of a radical-ion, and it is evidently this form which is detected by measurements of electron paramagnetic resonance (see below).

8. Formation of Free Radicals during Photoreduction

Oxidant molecules (quinones, nitro compounds) quench the fluorescence of chlorophyll, but do not react with it photochemically, whereas reducing agents, which do react, exert no "physically" extinguishing effect on the fluorescence of the pigment[61]. These observations indicate that it is possibly the metastable pigment molecules which take part in the reaction. These are, according to Terenin, G.N.Lewis, and Kasha, and as is now universally accepted, in a triplet or biradical state. The reversal of electron spin on the formation of the long-lived metastable level determines the continued existence of a "hole", a vacant electronic level formed as a result of the excitation of a pigment molecule.

In the elementary step of photoreduction an electron is taken up by an excited chlorophyll molecule from a donor molecule, which should be accompanied by formation of a pair of radical-ions; subsequent transfer of a proton can lead to the formation of a pair of radicals in non-ionic form:

$$X + AH_2 \rightleftharpoons {\cdot}X^- + {\cdot}AH_2^+ \rightleftharpoons {\cdot}XH + {\cdot}AH.$$

Uri[62] has noted that chlorophyll in the presence of ascorbic acid initiates the polymerisation of methyl methacrylate.

A detailed investigation[44,45] of the initiation of polymerisation by the pigment–hydrogen-donor system in pyridine solution and in aqueous emulsion has shown that polymerisation is initiated by chlorophyll and all its analogues and derivatives. Phycobilins, which are not subject to photoreduction, had no effect on polymerisation. The most active electron-donors were dienols, cysteine, and ferrous compounds. (Incidentally, we were unable to detect reaction between Fe^{2+} and chlorophyll by other methods.) Polymerisation was inhibited by compounds (e.g. safranine, riboflavin) which react vigorously with the photoreduced forms of the pigments.

Under anaerobic conditions polymerisation is evidently initiated by the radical-ion reduced form of the pigment, and by products of the photoreduction of oxygen (OH, HO_2) when the latter is present. In support of Rosenberg's remark[63] about the possible effect of the triplet state of the pigment in these experiments, it must be pointed out that active polymerisation was observed only in the presence of electron-donor molecules. Linshitz and Weissman[7] found no paramagnetic resonance with the "red" reduced form of chlorophyll, and it is not yet clear whether this form is a radical or a non-radical dismutation product XA_2. The second possibility must be regarded as the more probable. We have pointed out[58] that, if measurements of paramagnetic resonance are made during illumination of the chlorophyll–ascorbic acid system, an effect due to formation of radical-ions will be detected with a sufficiently sensitive apparatus. Measurements carried out soon after this showed[45] that illumination of chlorophyll–ascorbic or phaeophytin–ascorbic acid vacuum systems in the resonance machine, by a quartz mercury lamp, gave a signal, which immediately disappeared when the light was switched off. The signal was strongest for illumination of the phaeophytin–ascorbic acid system at -40°, i.e. under conditions favouring the formation of the radical-ion reduced form. In the absence of a reducing agent it was not possible to observe the effect.

As we have already mentioned, in the elementary photoprocess of electron transfer a pair of radical-ions is formed — the radical reduced form of the pigment ··X^- and the radical oxidised form of ascorbic acid ·AH^+, which in strong bases can be in the form of a negatively charged radical-ion.

Commoner[64] reported to the Fourth International Biochemical Congress that the structure of the electron-paramagnetic-resonance signal observed during the photoreduction of chlorophyll by ascorbic acid corresponds to the radical oxidised form of the latter. These conclusions are in agreement with data obtained in the Institutes of Chemical Physics and of Biochemistry of the Academy of Sciences of the USSR[65], where it has been shown that the signal has the same structure for the photoreduction by ascorbic acid of various pigments — chlorophyll, haematoporphyrin, phaeophytin, and magnesium-phthalocyanine (see Fig. 3). A

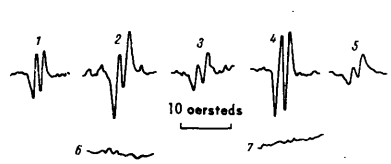


Fig. 3. Electron-paramagnetic-resonance spectrum produced during illumination of pigment–ascorbic acid system[65]: 1) chlorophyll *a*; 2) chlorophyll *a* + chlorophyll *b*; 3) phaeophytin *a* + phaeophytin *b*; 4) haematoporphyrin; 5) magnesium-phthalocyanine; 6) ascorbic acid without pigment; 7) chlorophyll without ascorbic acid.

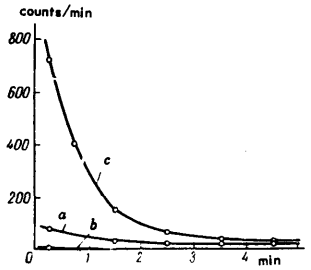


Fig. 4. Chemiluminescence produced during oxidation of photoreduced form of chlorophyll (measurements with photon counter)[69]: *a*) after illumination of the chlorophyll — ascorbic system in the absence of air; *b*) admission of air in the dark after photoreduction; *c*) admission of air and introduction of ammonia solution after photoreduction.

signal of the same structure is observed during the illumination of ascorbic acid in piperidine, yielding a coloured complex with this strong base. When other reducing agents (phenylhydrazine) are used, no signal can be observed, evidently because of the very small photostationary concentration of the radical reduced form of chlorophyll.

The oxidised form of ascorbic acid formed during photoreduction (monodehydroascorbic acid) is relatively stable, does not undergo rapid secondary reactions (dismutation, etc.) in basic media, and probably exists in the form of a radical-ion.

During this work an electron-paramagnetic-resonance signal of the same structure as in the photoreduction of chlorophyll was observed on illumination of the blades of certain grasses directly in the resonance machine.

9. Chemiluminescence during the Reverse Reactions of the Photoreduction Products of Chlorophyll

Strehler and Arnold[66] detected in green leaves and chloroplasts an extremely weak red afterglow, lasting for several minutes after the light had been switched off. Further investigation showed that the glow consists of several components of different duration. This feeble glow could be detected by means of a photon counter, a photomultiplier cooled in liquid nitrogen serving as collector.

To get an idea of the nature of the glow observed in leaves, it is desirable to investigate all types of chemiluminescence exhibited by chlorophyll. Thus a red glow accompanying the oxidation of chlorophyll and its analogues with tetralin peroxide has been known for a long time[67,68].

By means of the photon counter, chemiluminescence could be observed during the reversible oxidation of chlorophyll which had been photoreduced with ascorbic acid[69]. After illumination of a pyridine solution of chlorophyll containing ascorbic acid or phenylhydrazine, the reverse reaction (in the dark) is accompanied in the absence of air by an extremely feeble afterglow. Admission of air increases the effect by accelerating the reverse reaction. Introduction of ammonia, which greatly accelerates the reverse reaction of the "red" photoreduced form of chlorophyll[20], also leads to a very great intensification of the luminescence effect[69] (see Fig. 4).

In the absence of reducing agent no glow is observed under these experimental conditions. The mechanism of the process requires investigation; it may be that the dark reaction between the reduced form of chlorophyll and oxygen is accompanied by the formation of a biradical, a triplet state. At the expense of the heat content of the system, this passes into an excited singlet state which emits a glow spectrally similar to the fluorescence:

$$XH_2 + O_2 \rightarrow XH_2{\cdot}O_2 \rightarrow {\cdot}X{\cdot} + H_2O_2,$$

$$\cdot X\cdot \rightarrow X^* \rightarrow X + h\nu.$$

Excited states can be formed also during the reverse reactions of the radical-ion photoproducts:

$$\cdot XH + \cdot AH \rightarrow X^* + AH_2; \quad X^* \rightarrow X + h\nu.$$

Further work should show whether the long-lived glow in Strehler and Arnold's experiments can be attributed to the oxidation of chlorophyll or of its photoreduced form.

10. Formation of Association Complexes before Reaction

Contact between the reactant molecules is a condition for the occurrence of the primary photoprocess; the duration of this contact may vary. The life of the "active complex" at the moment of collision is very brief, but the formation of long-lived association complexes is also possible, these breaking down after the occurrence of electron transfer.

In our case three types of association with a hydrogen-donor molecule are conceivable, formed respectively with the pigment molecule in its ground state, with an excited molecule in a singlet state, or with a long-lived excited molecule in a triplet state.

The formation of long-lived complexes of chlorophyll with ascorbic acid in pyridine medium is unlikely, since the molecules of the medium (a base) themselves coordinate with the central magnesium atom of the chlorophyll molecule[70]. In fact, the introduction of ascorbic acid into a pyridine solution of chlorophyll does not affect its absorption spectrum. However, the formation of short-lived complexes, in which electron transfer occurs, is possible. On the other hand, Dain and his collaborators[28] observed a change in the absorption spectrum when chlorophyll reacts with metal ions, which, in the opinion of these workers, indicated the formation of long-lived complexes.

The formation of complexes with a molecule in an excited singlet state could probably be ascertained by measuring the half-life $\tau_{1/2}$ of the excited state of the pigment when an ascorbate or other hydrogen-donor is introduced; such experiments have evidently not been carried out.

Similar experiments could be made with pigments in the triplet state, the great chemical activity of which[71] is responsible for their tendency to form complexes.

The experiments of Evstigneev and Gavrilova[111] have shown that the rate of formation of the primary photoreduced form of phaeophytin is independent of temperature if the viscosity of the medium does not change greatly; if, however, the viscosity is increased by introducing glycerol, the rate of reaction falls. When the solution is frozen, no reaction takes place; these workers consider that kinetic

collisions are necessary for reaction to occur, and the existence of complexes long-lived is unlikely when not illuminated.

11. Mechanism of Photoreduction

Using Michaelis' hypothesis of a "one-electron" mechanism for oxidation–reduction reactions, we suggested[1] a scheme for the process consisting of the following stages:

1. Absorption of an electron by an excited (probably a metastable biradical) pigment molecule X from a hydrogen-donor molecule AH_2 with formation of a pair of radical-ions. We have pointed out the probability of the absorption of an electron by the cyclic system of conjugated double bonds of the pigment molecule (see scheme in Fig. 5):

$$X + AH_2 \rightleftharpoons \cdot X^- + \cdot AH_2^+; \quad \cdot AH_2^+ \rightleftharpoons \cdot AH + H^+.$$

2. Transfer of a proton combined with the molecules of the basic medium, with formation of a pair of radicals and subsequent formation of non-radical compounds:

$$\cdot X^- + \cdot AH_2^+ \rightarrow \cdot XH + \cdot AH \rightarrow XH_2 + A.$$

The experimental results support the main features of this scheme.

A summary of the main experimental results (described in the preceding sections of the review), supporting this reaction mechanism, is given below.

Experimental results	Consequence
1. Reversible photoreduction is shown by all pigments having a porphin, chlorin, bacteriochlorin, or azaporphin structure (with H, Mg, or Zn at the centre of the molecule), independently of the nature of the side groups.	The existence in the pigment molecule of a cyclic system of conjugated double bonds linking the four pyrrole nuclei is an essential condition for reaction.
2. The basic strength of the medium in which reaction occurs strongly influences the spectral properties and the reactivity of the products of the photoreduction.	The various types of photoreduction products are linked by acid-base equilibria (proton transfer).
3. On illumination of a pigment–hydrogen-donor system the potential of an inert electrode becomes more negative and the electrical conductivity of the system increases.	Products which are ionic in character are formed, together with reactive photoproducts, which give up an electron to the electrode.
4. Illumination at low temperature inhibits the formation of stable photoreduction products; under these conditions the reversible primary process occurs rapidly, accompanied by the effects indicated in the previous paragraph.	The reaction includes a photochemical stage of electron transfer and a dark stage.
5. When deuterated hydrogen-donors are used, the dark stage of the reaction is slowed down.	The dark stage is associated with proton transfer.
6. On illumination, the pigment–hydrogen-donor system initiates the photopolymerisation of methyl methacrylate. During illumination of the pigment–hydrogen-donor system the appearance of an electron-paramagnetic-resonance spectrum is observed: this vanishes after the light has been switched off.	Reaction is accompanied by the formation of photoproducts which are of the nature of free radicals (or radical-ions).

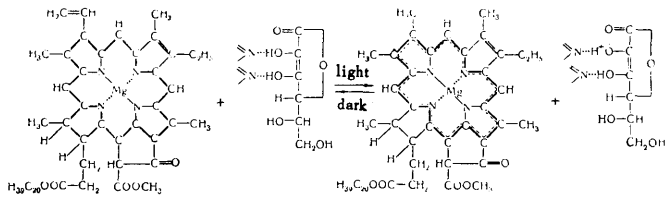


Fig. 5. Photoreduction of chlorophyll with ascorbic acid. The heavy line shows one of the possible cyclic paths of conjugation of the system of double bonds of the chlorophyll molecule. The dotted line shows the absorption of an electron by the system of conjugated bonds of an excited chlorophyll molecule; $\gtrdot N$ represents molecules of the basic medium, linked by a hydrogen bond to the reactant molecules.

When conditions are such that the dark stages of the reaction, associated with transfer of a proton (hydrogen), are inhibited, electron transfer is observed in its "pure" form. In media of different basic strength different protolytic equilibria are established. The dependence of the spectral properties of the photoproducts on the nature of the medium is especially clearly observed with the porphyrins, in which various stages of acid–base equilibrium are possible owing to the presence of acidic (carboxyl) and basic (pyrrole nitrogen) groups. The number of protons added to the molecule and the number of electrons transferred are not in general the same, and the photoproducts may be cationic or anionic in character, as can be seen from the marked differences in the properties of the photoreduced forms of haematoporphyrin in different media, from strong bases (piperidine) to strong acids (an aqueous solution of sulphuric acid).

Further studies of the structure of the paramagnetic-resonance bands of the photoproducts will probably make possible the location of the electron and the proton in the pigment molecule.

II. OXIDATION–REDUCTION REACTIONS PHOTOSENSITISED BY CHLOROPHYLL

When a chlorophyll–electron-donor–electron-acceptor system is illuminated with red light, a sensitised reduction of the acceptor molecules is observed, brought about by the light quanta absorbed by the chlorophyll[72]. This property is possessed by all the chlorophyll analogues studied (including magnesium-phthalocyanine) which can undergo photoreduction. With bacteriochlorophyll and bacteriophaeophytin the reactions are activated by near infra-red radiation[73,74].

The course of the reaction can be conveniently followed by means of spectrophotometric measurements in Tunberg vacuum tubes, either the change in optical density at the absorption maxima of the acceptors or the development of new maxima of the reduced compounds being observed.

Using ascorbic acid (E_0 = +0.05 V) as electron-donor, we observed the photoreduction of riboflavin (E_0 = -0.22 V), safranine T (E_0 = -0.3 V), and pyridine nucleotides (E_0 = = -0.32 V). When the light is switched off, the reverse reactions take place at a different rate, sometimes requiring the introduction of oxygen to regenerate the dye from the leuco form.

During these reactions the energy of the light is "stored", there being an increase in the free energy of the system, characterised by the value of ΔE_0 for the donor ($E_0 = +0.05$ V) and the acceptor ($E_0 = -0.32$ V) of the electron; a rough estimate of the stored free energy can be made: $\Delta F = 2 \times \times 23.06 \times 0.4 = 18.4$ kcal.

The comparative slowness of the reverse reactions in these processes is to be explained by the rapid dismutation of the semiquinones first formed to leuco compounds; during exposure the rate of dismutation is greater than the rate of the reverse reactions of the primary photoproducts.

We were able to observe the chlorophyll-sensitised oxidation–reduction of cytochrome *c* in aqueous medium [25,26]; in this reaction proteins (water ?) could serve as electron-donors. Photooxidation of the reduced cytochrome was carried out in the presence of atmospheric oxygen.

When azo dyes are employed as electron-acceptors, they undergo irreversible reduction; the azo dye methyl red has been used for a long time in reactions of this type [75,76]. However, reduction of methyl red by ascorbic acid and phenylhydrazine occurs slowly and in the dark, the reaction being very greatly accelerated by light.

In several sensitised reactions which occur under aerobic conditions, oxygen is the ultimate electron-acceptor. The chlorophyll-sensitised oxidation of several organic compounds has been known for a long time, but hitherto there has been no single view as to the mechanism of this process. The photooxidation of several hydrogen-donors, capable of the photoreduction of chlorophyll and phaeophytin, has been observed by means of Warburg's manometric method [77,78]. Probably in this case also, the dark stage of the reaction is in effect the regeneration of chlorophyll from the intermediate photoreduced form by oxidation with oxygen. The alternative mechanism of the primary photochemical formation of a peroxide of chlorophyll, which is reduced in the dark by the hydrogen-donor, is less probable, although we have detected labile photooxidation products of chlorophyll and bacteriochlorophyll, which slowly react with ascorbic acid to regenerate the pigment [17,79,80]. The photoreduction of chlorophyll by a hydrogen-donor is far more rapid than the photochemical reaction with oxygen.

That the sensitised reactions under investigation pass through a stage of reversible photoreduction of the sensitising pigment is suggested by the following facts:

1. Sensitised reduction is observed in a system containing hydrogen-donors which can take part in the photoreduction of chlorophyll.
2. Accumulation of the photoreduced forms of the pigments cannot be observed in a ternary system containing an electron-donor, a pigment, and an electron-acceptor, owing to the rapid reaction of the photoreduced forms with the acceptor molecules; only after the whole of the acceptor has undergone "sensitised" reduction does formation of the photoreduced form of the sensitising pigment begin. This is shown as an induction period in the sensitised reactions (cf. ref.21).
3. Finally, it is possible to carry out separately the photochemical stage of the reaction (formation of photoreduced forms of the pigment) and their dark reaction with the electron-acceptor molecules. In the case of chlorophyll this is illustrated by the experiments with the "red" photoreduced form [38], whereas the "primary" photoreduced forms react with acceptors far more rapidly, as was shown by Evstigneev's experiments [13]. Extremely significant facts are the effect of acceptors on the photopotential of an electrode in the chlorophyll–ascorbic acid system [28] and the "damping" effect of these compounds on the photoconductivity of this system [81], due to their rapid reaction with the photoreduced form of chlorophyll.

Thus experimental facts support the conclusion that the sensitised reactions occur via a stage of reversible photoreduction of chlorophyll and its analogues. The mechanism of sensitisation, established in experiments with chlorophyll, is similar to the scheme put forward by Weiss [82] more than twenty years ago for sensitising dyes which form leuco compounds.

In our laboratory a detailed investigation has been made of the part played by the photoreduced forms of pigments in sensitised reactions, but a more profound study is required of the role in these reactions of the "semi-oxidised" forms of electron-donor molecules of the type of monodehydroascorbic acid, the steady-state concentration of which is quite high, as is shown by electron-paramagnetic-resonance measurements.

These "semi-oxidised" compounds are evidently capable not only of the reverse reactions with the reduced forms of the pigment but also of further oxidation (to dehydroascorbic acid), by transferring their hydrogen to an acceptor — a molecule of oxygen, methyl red, etc. However, the limits of the reducing power of these compounds are obscure: they can hardly reduce systems having such a potential as high as that of safranine or the pyridine nucleotides.

Thus the mechanism of the transfer of hydrogen from a molecule AH_2 to a molecule B, sensitised by chlorophyll or its analogues, can be represented by the following scheme:

1. Photoreduction:

$$X + AH_2 \rightleftharpoons \cdot X^- + \cdot AH_2^+ \rightleftharpoons \cdot XH + \cdot AH.$$

2. Dark stages of the reaction with the hydrogen-acceptor (electron-acceptor) B; regeneration of chlorophyll from photoreduced forms:

$$\cdot X^- + B \rightarrow X + \cdot B^-; \quad \cdot B^- + H^+ \rightarrow \cdot BH.$$

$$\cdot XH + B \rightarrow X + \cdot BH; \text{ possibly also } \cdot AH + B \rightarrow A + \cdot BH.$$

3. Dismutation of semiquinone forms:

$$2 \cdot BH \rightarrow B + BH_2.$$

Overall process:

$$AH_2 + B + (X) \rightarrow A + BH_2 + (X).$$

Such a reaction mechanism has received direct experimental verification in solution, but with heterogeneous sensitisation on pigment crystals and in colloidal solutions it is extremely difficult to separate the individual stages of the reaction occurring at the phase boundary. It may be assumed that the elementary steps of electron transfer from acceptor to pigment molecule (hole") at the phase boundary and the compensating transfer of an electron to the acceptor molecule are retained here too. We have indicated the possibility of such a mechanism in studying the photocatalytic action of heterogeneous sensitisers [83,84]. The experiments of Evstigneev and Terenin on the photopotentials of solid films of pigments in aqueous media also suggest this [85].

III. PHOTOCHEMICAL REACTIONS OF COLLOIDAL SOLUTIONS OF CHLOROPHYLL

Reactions of the chlorophyll molecule in organic solvents have been described above; we shall now examine the properties of chlorophyll in aggregated forms, in aqueous colloidal solutions.

It has long been known that such colloids are formed by running solutions of chlorophyll (in alcohol, acetone, dioxan, pyridine) into an excess of water or of a buffer solution. We have found that colloidal solutions of chlorophyll are obtained also by the direct dissolution in water of a chromatographic band of chlorophyll adsorbed on sugar. The position of the absorption maximum and the particle size depend on the type of solvent and the pH of the aqueous medium; at pH 4–5 coarser particles are formed having maximum absorption at 690 mμ, and at pH 8–9 extremely stable colloids result with a maximum at 670–672 mμ [86]. In contrast to these systems, we have found that colloids obtained by running solutions of chlorophyll into aqueous solutions of detergents (anionic, cationic, and non-ionic) possess a bright fluorescence, an absorption maximum at 669–670 mμ, and photochemical properties similar to those of chlorophyll in solution [77,87]. This is probably due to the fact that the pigment molecules are arranged in the form of a monolayer on the detergent micelle, i.e. they are in a dispersed form.

Colloidal solutions of chlorophyll in water possess a photosensitising action, which is most marked if the ultimate electron-acceptor is reduced irreversibly, as occurs with oxygen and azo dyes (methyl red). In some experiments the polymerisation of acrylamide was observed on illuminating aqueous colloidal solutions of chlorophyll with red light and in a vacuum.

In contrast to the comparatively feeble activity of these systems, colloids obtained using detergents have a strong sensitising action, as great as that of chlorophyll in solution. Doubtless the fundamental mechanism of the process in solution is retained here. The photosensitising action of coagulated colloidal chlorophyll has been described in recent papers from our laboratory [88].

IV. PHOTOCHEMICAL PROPERTIES OF CHLOROPHYLL IN THE GRANULES OF CHLOROPLASTS

The properties of the chlorophyll in granules were studied in viscous aqueous glycerol media, which permitted accurate spectrophotometric measurements as a result of their transparency and their "colloidal" stability. Such systems permit work to be carried out also at low temperatures.

Such "green solutions" of leaves of the sugar beet containing an ascorbate showed on illumination small reversible changes (up to 3%) in the optical density in the red absorption maximum of chlorophyll, which are attributable to reversible photoreduction; changes to more negative values were also observed in the photopotential of an inert electrode. With a Beckman spectrophotometer we were unable to detect any definite changes in optical density at 520 mμ. In the absence of ascorbate, effects of smaller magnitude were observed. Such reversible photochemical changes in homogenates of green leaves are to be ascribed to the "monomeric" form of chlorophyll, which has closely similar properties to those of chlorophyll in solution [86,89,90].

It is well known that in an "oxidising" medium homogenates of leaves show Hill's reaction, i.e. evolution of oxygen coupled with reduction of the oxidising agents — Fe^{3+}, quinones, etc. In a "reducing" medium, in the presence of sodium ascorbate, homogenates of leaves are capable of reversible photosensitised reduction of safranine and other compounds and also of irreversible reduction of oxygen and methyl red [91].

Leaves of plants possessing a large amount of the rapidly decolorised monomeric form are more active in reactions of this type; e.g. leaves of the sugar beet are more active than leaves of the bean.

The biological role of the different forms of chlorophyll and the part they play in the reactions of photosynthesis is not yet clear. It has been estimated that the transfer of a single electron from water to carbon dioxide requires about two quanta of red light, and this may possibly require two types of photochemical reactions with a reserve of intermediate compounds between them. Different types of reactions are possibly associated with different forms of chlorophyll. In any case, the ability of a chlorophyll molecule to take up an electron when illuminated is retained in the "collective" of molecules in aggregated forms. The transfer of energy between the pigment molecules in such aggregates (in the granules of plastids) can probably occur in the form of a "hole" and an unpaired electron, and at the level of the triplet state, e.g. by the mechanism suggested by Terenin and Ermolaev [92,93].

V. REVERSIBLE PHOTOCHEMICAL CHANGES UNDERGONE BY CHLOROPHYLL IN THE LIVING PLANT LEAF

Special methods are required for recording the rapid reversible changes undergone by chlorophyll during the photochemical reactions occurring in the living leaf. Techniques used for this purpose at present are differential spectrophotometry, and flash photolysis, fluorescence, and electron paramagnetic resonance.

Coleman et al. [94] were able to observe reversible changes in the red absorption maximum of chlorophyll in a suspension of *Chlorella*, and also in the vicinity of 520 mμ, which can be attributed to reversible photoreduction. In a subsequent paper Coleman and Rabinowitch [95] pointed out the similarity in the differential spectra after illumination of a suspension of *Chlorella* and after the photoreduction of chlorophyll with ascorbic acid; arguments are given for the occurrence of the reversible photoreduction of chlorophyll in living organisms. The fact requires explanation, however, that in the photoreduction of chlorophyll the ratio of the fall in optical density in the red absorption maximum ($\Delta D_{670\ m\mu}$) to the increase in density in the maximum of the photoreduced form ($\Delta D_{520\ m\mu}$) has a value of 2–3, whereas in *Chlorella* cells this ratio hardly reaches unity. In Witt's experiments [96], in which a flash technique was employed, the fall in the optimum density in the red absorption maximum corresponded to the reversible fall in the red fluorescence of chlorophyll and the appearance of a maximum at 520 mμ.

The appearance of this maximum after living leaves have been illuminated was first discovered by Duysens [97], and subsequently studied by Witt [96], Bell [98], and other workers. The agreement between this maximum and the absorption of the "red" photoreduced form of chlorophyll is remarkable.

The experiments of Osipova and Timofeeva [99] have shown a high content of basic amino-acids in the proteins of the granules; on the basis of these results, Rackow and Konig [9] have pointed out the possibility of detecting the photoreduced form of chlorophyll in Witt's experiments. It is not clear,

however, whether the ratio between the fall in optical density in the red absorption of chlorophyll and in the maximum at 520 mμ, observed during photoreduction, is maintained in these experiments. Clearly, the conditions of acid–base equilibrium in chloroplasts may differ greatly from those in pyridine solutions, and reversible photoreduction of chlorophyll may occur also without the accumulation of the "red" form[91].

Although the nature of the absorption maximum appearing at 515–520 mμ in leaves cannot yet be regarded as cleared up, it is highly probable that the reversible change in the red absorption maximum of chlorophyll can be ascribed to photoreduction.

Use of fluorescence spectroscopy will probably be of great help in ascertaining the nature of the changes undergone by chlorophyll in leaves. Measurements by Litvin[100] have shown the presence in living green leaves of fluorescence maxima within the range of the photoreduced forms of chlorophyll, but it is still difficult to interpret these results. It is also necessary to determine whether the phenomenon of a separate stage of photoreduction of chlorophyll is connected with the appearance of the paramagnetic-resonance bands observed by Commoner[101] and later by Calvin and his collaborators[102].

The phenomenon of chemisynthetic luminescence, observed in the leaves of plants, suspensions of chloroplasts, and solutions of chlorophyll, indicates that similar photoproducts may be formed in all these cases.

VI. REVERSIBLE PHOTOREDUCTION AND POSSIBLE MECHANISM OF THE PARTICIPATION OF CHLOROPHYLL AND ITS ANALOGUES IN PHOTOBIOLOGICAL PROCESSES

The above account has shown that chlorophyll and porphyrin pigments in general have the characteristic ability to undergo reversible photochemical reduction, the reversible absorption of an electron (or hydrogen) from donor molecules. We have already put forward the hypothesis that this may play a part in separate stages of the participation of chlorophyll and its analogues in the reactions of photosynthesis and other photobiological phenomena.

1. Photosynthesis[112]

The work reported above has established that the photosynthesising action of chlorophyll in reactions involving the photochemical transfer of hydrogen (or an electron) is determined by its ability to undergo reversible photoreduction.

In the actual photochemical step an excited pigment molecule takes up an electron (hydrogen) from the donor molecule, and in the dark stage it transfers the electron to the acceptor molecule. These results make it possible to set up the working hypothesis that during photosynthesis chlorophyll also takes part in the reversible transfer of an electron (raising it above the level of the reduced pyridine nucleotides), in agreement with several investigations which have shown the possibility of the photoreduction of pyridine nucleotides in suspensions of chloroplasts and in the leaves of plants[103–105].

The suggestion that chlorophyll takes part in an electron-transfer process with the intermediate formation of free radicals accords with the results of measurements of electron-paramagnetic-resonance in chloroplasts and in leaves[101,102] and with observations on the presence of an extremely feeble long-lived afterglow (chemiluminescence) after leaves have been illuminated[66].

The experimental results which have now accumulated indicate that the operation of the cycle of enzymic reactions for the reduction of carbon dioxide necessitates the photochemical formation of reduced pyridine nucleotides and energy-rich phosphate esters.

The photochemical transfer of an electron (hydrogen) "upward" to the level of reduced pyridine nucleotides makes possible the operation of the carbon dioxide assimilation cycle according to Calvin's scheme[106]. The formation of the energy-rich phosphate esters required for the functioning of the carbon dioxide reduction cycle occurs, according to the work of Arnon[107], by anaerobic photosynthetic phosphorylation, in which adenosine triphosphate is formed from adenosine diphosphate and inorganic phosphate by oxidation–reduction processes — dark reactions activated by photoproducts, involving biocatalytic systems — cytochromes, naphthoquinone derivatives (vitamin K), etc. Thus the "downward" drop of the photochemically mobilised electron makes possible phosphorylation and the "storage" of energy in adenosine triphosphate.

2. Photodynamic Action of Porphyrins

The basis of this phenomenon is the dye-photosensitised photooxidation of metabolites or proteins of importance in vital processes, leading to the haemolysis of erythrocytes and a series of far reaching disturbances of the normal functioning of organisms[108]. The mechanism of the primary photochemical process underlying the photodynamic effect is not yet clear. The investigations of the mechanism of the photosensitising action of porphyrins discussed here provide a basis for the hypothesis that the primary stage in this process is photoreduction of the pigment. Thus our work has established the ability of porphyrins to undergo reversible photoreduction by dienols, cysteine, and several other organic compounds.

Oxidation of the photoreduced forms of porphyrins by oxygen or other oxidising agents leads to the reverse process of the regeneration of the original pigment molecule. In this process, as in the case of chlorophyll, the radical-ion forms of the pigment are the most active. It may be assumed that the mechanism of the separate steps in the photodynamic effect corresponds to the scheme of reactions photosensitised by porphyrins given above (see Part II); AH_2 represents a molecule of the metabolite undergoing oxidation (a protein amino-acid, etc.), and X a molecule of the porphyrin pigment.

3. Other Photobiological Reactions

Study of various photobiological processes — photoperiodism, germination of seeds under the influence of light, etc. — in the work of Bortwick, Hendricks, et al.[109] led to the discovery of a maximum in the activating spectrum at 650 mμ; the effect of red light was cancelled by subsequent illumination with an effective spectral maximum at 740 mμ. These observations led the authors to the hypothesis that a pigment system is present, which undergoes reversible photochemical changes with the formation of photoproducts possessing absorption maxima at 650 and 740 mμ.

It has not yet proved possible to find transitions of this type in pigments in plants. We have already pointed out above that the reversible photoreduction of porphyrins can be observed, leading to the formation of photoproducts having maximum absorption at 740 mμ; it is significant that infra-red irradiation accelerates the reverse reaction of these photoproducts [110].

It is possible that the reversible formation of photoreduction products of porphyrin pigments may play a part also in several photobiological processes of this type.

CONCLUSION

Chlorophyll and its analogues and derivatives undergo reversible photochemical reduction. During this reaction photoproducts which store the light energy are formed; in the dark stage of the process these photoproducts undergo the reverse reactions, leading to the formation of the original pigment molecule. The ability of chlorophyll and its analogues to undergo reversible photoreduction underlies the photosensitising action of these pigments in oxidation–reduction reactions.

The experimental results obtained provide a basis for the working hypothesis that the ability of chlorophyll and its analogues to undergo reactions involving photochemical electron (or hydrogen) transfer may be linked with the part played by these pigments in photobiological processes.

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PHYSICOCHEMICAL PROPERTIES OF CHLORINE TRIFLUORIDE

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INTRODUCTION

Elemental fluorine can now be made in large quantities and this has facilitated the study of the physical and chemical properties of a number of inorganic fluorides. Among these halogen fluorides are of great theoretical and practical interest. Emeléus and Woolf [1], have shown that the halogen fluorides are ionising solvents which dissociate according to the equation

$$2MF_n \rightleftharpoons MF_{n-1}^{+} + MF_{n+1}^{-}.$$

The physical and chemical properties of the halogen fluorides can be explained by considering them as self-ionising solvents. The great experimental difficulties associated with the handling of these highly reactive compounds did not permit reliable determinations of their physical constants until recently. Table 1 gives some physical properties of known halogen fluorides (figures for elemental fluorine are given for comparison) [2-41].

All the halogen fluorides are powerful fluorinating agents and it is interesting to consider their chemical properties from this point of view. The compounds can be arranged in the following order of reactivity: $ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5 > BrF$, although in a number of cases the characteristics of the halogen fluorides as fluorinating agents are known only qualitatively. Chlorine trifluoride is the most reactive of the known halogen fluorides.

The halogen fluorides are of practical importance as fluorinating agents in the preparation of a number of higher fluorides [21-24] and especially of uranium hexafluoride, used in the regeneration of nuclear fuel [25-28]. Complete combustion of the fuel is not achieved in atomic reactors. Consequently several combustion cycles with intermediate regeneration cycles are necessary for its complete utilisation. Fractional distillation is the most suitable method for regenerating nuclear fuel because the technology of this process has been well developed and uranium is regenerated

TABLE 1. Some physical properties of halogen fluorides and fluorine.

Halogen fluoride	m.p., °K	b.p., °K	Heat of formation, kcal mole^{-1}	Conductivity at 25°, ohm^{-1} cm^{-1}	Trouton's constant	Fluorine content, %	Density at 25°, g cm^{-3}
ClF_3	196.84	284,79	37.9+1.0	3.10^{-9}(0°)	20.8	61.62	1.8094
ClF	119	172	13.3±2.1	—	28.0	34.86	—
BrF_5	212.7	313.94	—	$9.1\cdot10^{-8}$	23.2	54.28	2.460
BrF_3	281.93	398.83	75	$8.0\cdot10^{-3}$	25.7	41.60	2.8030
BrF	240	293	18,4±0 5	—	20.5	19.19	—
IF_7	278	277 sublimes	—	—	<26.4	51.15	2.75
IF_5	282.61	373.64	204 7	$5.4\cdot10^{-6}$	27.2	42.79	3.19
F_2	55	86	—	—	—	100.0	—

directly as UF_6 by this method. This compound is advantageous when the regenerated uranium has to be passed to a diffusion plant for concentration[26]. Substantial differences between the volatility of a number of fluorides of fission products and that of uranium hexafluoride enable the latter to be easily purified by fractional distillation[26,27]. The initial attempts to fluorinate uranium metal with elemental fluorine were unsatisfactory, because it was difficult to remove the large quantity of heat evolved in the heterogeneous reaction

$$U(solid) + 3F_2(gas) = UF_6(gas),$$

and in practice the reaction could not be controlled. A practical solution of this problem was found in the use of liquid fluorinating agents, such as the halogen fluorides. These are very suitable because of the range of temperature over which they remain liquid (see Table 1).

The preceding account explains the great interest that has been shown in the halogen fluorides in recent years. Published reviews[29-34] on chlorine trifluoride are largely out of date because of the intensive investigations on these compounds in recent years. None of the reviews deal with the study of systems based on chlorine trifluoride, since investigations on these systems have been carried out and published only recently in connection with the work of the Second International Geneva Conference on the Peaceful Uses of Atomic Energy[35]. This review is devoted to the physical and chemical properties of chlorine trifluoride, the most reactive of the known halogen fluorides.

1. PREPARATION OF CHLORINE TRIFLUORIDE

Chlorine trifluoride, ClF_3, was first prepared in 1930 by Ruff and Krug[15,36], in an apparatus which had been previously used for the synthesis of chlorine monofluoride, ClF.[15,36] Gaseous fluorine and chlorine were led into a heated copper vessel, where they reacted to form chlorine monofluoride and chlorine trifluoride. Three receivers, the first two of quartz and the third of glass, were attached to the reaction vessel. The first receiver, maintained at -70°, served to condense ClF_3; the second, cooled to -150°, was intended to entrain ClF, and the third, surrounded by liquid air, was used to freeze out the excess of fluorine. A copper or glass tube filled with ignited potassium fluoride was attached to the outlet of the third receiver to keep out atmospheric moisture.

The literature on methods of preparation of ClF_3 is practically confined to this work[15]; later papers merely indicate some improvements in the process. For example, ClF_3 has been prepared by the reaction of fluorine and chlorine in a nickel vessel at 280°.[2,13] Pilot-scale production of ClF_3, for use as an incendiary material, was organised in Germany during the Second World War; the method comprised heating a mixture of fluorine and chlorine with a nickel catalyst[37].

Some information on the synthesis of ClF_3 in an experimental pilot plant made of monel metal has also been published[38]: the ClF_3 was prepared by heating a stoichiometric mixture of fluorine and chlorine to 300°. The reaction products were condensed in a helical condenser before passing to a receiver. Condensed chlorine trifluoride can be stored for long periods in steel cylinders[38]. Besides nickel and monel metal, copper can be used in the construction of plant for the production of ClF_3.[15]

2. PHYSICAL PROPERTIES OF CHLORINE TRIFLUORIDE

Under normal conditions chlorine trifluoride is a colourless gas with a molecular weight of 92.457. The melting point is given as -83°[15] and -82.6°[39] in early papers on ClF_3; these values were incorrect and it was later shown that ClF_3 melts at -76.32 ± 0.05°;[2] this conclusion was reached from an examination of the melting point of three samples of ClF_3 containing 0.04, 0.3, and 1.8 mole % of impurities (Fig. 1).

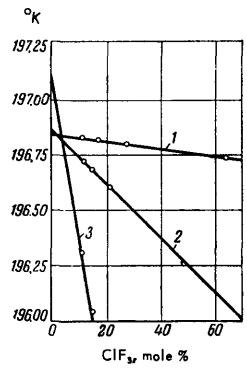


Fig. 1. Determination of the melting point of chlorine trifluoride of different degrees of purity. Impurities: 1) 0.004 mole %; 2) 0.3 mole %; 3) 1.8 mole %.

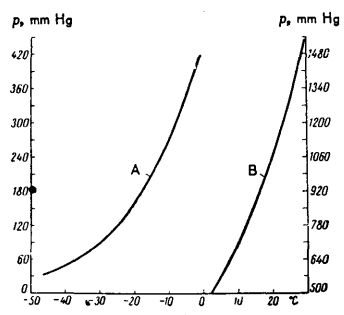


Fig. 2. Vapour pressure of chlorine trifluoride from 0 to 1550 mm Hg.

TABLE 2. Molar heat capacity of chlorine trifluoride,

Temperature, °K	Molar heat capacity, cal mole^{-1} deg^{-1}	Temperature, °K	Molar heat capacity, cal mole^{-1} deg^{-1}	Temperature °K	Molar heat capacity, cal mole^{-1} deg^{-1}
solid		solid		liquid	
14.04	1.03	88.44	11.49	196.84	26.68*
16.60	1.50	95.62	12.03	202.76	26.76
20.10	2.13	103.44	12.47	204.83	26.78
25.88	3.36	111.35	13.03	207.69	26.81
32.59	4.75	126.54	14.16	216.53	26.94
40.67	6.22	141.87	15.28	219.84	26.96
45.88	7.05	156.22	16.28	226.95	27.05
56.27	8.39	171.20	17.36	237.83	27.22
62.67	9.07	180.60	18.04	248.6	27.38
67.82	9.60	184.96	18.46	259.30	27.61
78.96	10.62	196.84	19.18	269.86	27.84
				278.25	28.02

* Values obtained by extrapolation.

The boiling point of ClF_3 was first determined by Ruff and Krug[15] from an empirical relation between the vapour pressure and the temperature:

$$\log P \text{ (mm Hg)} = 7.42 - \frac{1292}{T}.$$

The boiling point found was 11.3°. Values of 12.1°[39] and 12.0° ± 0.1°[16] have also been reported. The vapour pressure–temperature relationship for ClF_3 was later expressed by the equation[2],

$$\log P \text{ (mm Hg)} = 7.3671 - \frac{1096.917}{t + 232.75}.$$

This yields a boiling point of 11.75°, lying between the values given above.

Fig.2 gives data on the vapour pressure of ClF_3. Trouton's constant, according to the equation derived by Ruff and Krug[15], is 20.8 cal deg^{-1} mole^{-1}. Schmitz and Shumacher[40] assume a value of 24.1 cal deg^{-1} mole^{-1} for Trouton's constant, but they do not indicate how this figure was obtained. The critical temperature of ClF_3 as determined by different authors, is close to 154°[15] or 174°;[2] the calculated critical pressure is 57 atm.[2]

The heat capacity of ClF_3 has been measured from 14°K to the boiling point; Table 2 gives heat capacities of solid and liquid ClF_3. It should be noted that the values in this Table have been corrected by the method of Hoge[41] for the heat capacity of the saturated vapour.

The heat of formation of ClF_3 can be found from the heat of formation of ClF and the heat of the reaction

$$ClF + F_2 = ClF_3,$$

for which determinations by independent methods have given the following results: 27.0 ± 1.5, 26.5 ± 0.5, and 25 ± 2 kcal × × mole^{-1}.[42,43] Greenwood[31] accepts 26.5 ± 1 kcal mole^{-1} as the heat of reaction between fluorine and chlorine monofluoride. From this value and the heat of formation of ClF (12.3 ± 1 kcal × × mole^{-1} [44]), the heat of formation of gaseous ClF_3 from the elements,

$$\frac{1}{2}Cl_2 + \frac{3}{2}F_2 = ClF_3,$$

can be found; the actual value is 38.8 ± 2 kcal mole^{-1}. Other data on the heat of formation of ClF_3 have been obtained by combining the data of Schmitz and Shumacher[42] for the reaction

$$ClF \text{ (gas)} + NaCl \text{ (solid)} = NaF \text{ (solid)} + Cl_2 \text{ (gas)}$$

with the data for the same reaction with ClF_3. Two values, depending on the value taken for the heat of formation of ClF, have been obtained for the heat of formation of ClF_3, 32.1 and 36.3 kcal mole^{-1}.[20] The most accurate value is 37.9 ± 1.0 kcal mole^{-1}.[20]

The density of liquid ClF_3 at the boiling point, first measured by Ruff et al.[45], is 1.77 g/cm^3. Banks and Rudge[16] give much more accurate values; they studied the density of liquid ClF_3 under the pressure of its own vapour over the temperature range -5° to +46° and derived the following relationship between the density and the temperature:

$$d_4^t = 1.8853 - 2.942 \times 10^{-3} t - 3.79 \times 10^{-6} t^2.$$

Table 3 gives values for the viscosity of ClF_3, determined by Banks, Davis, and Rudge[46]. The surface tension of ClF_3, determined by the capillary method, is expressed by the equation[46]

$$\gamma = 26.7 - 0.16t \pm 0.2 \text{ dyne cm}^{-1}.$$

Rogers and Garver[47] studied the viscosity and surface tension of the halogen fluorides and put forward the hypothesis that the high surface tension is due to the presence of "fluoride" bonds, similar to hydrogen bonds, the F^- ion playing the part of the proton in the hydrogen bond. The strength of these bonds decreases in the order $BrF_3 > IF_5 > > BrF_5 > ClF_3$.

The conductivity of liquid ClF_3 at 0° is 3×10^{-9} ohm$^{-1} \times \times$ cm^{-1}.[31]

Schmitz and Shumacher[42] first measured the thermal dissociation of ClF_3;[42] the reaction was carried out in a nickel vessel and the pressure measured with a sensitive quartz manometer. Table 4 gives values for the equilibrium constant of the reaction

$$ClF_3 \rightleftharpoons ClF + F_2$$

for different temperatures. The degree of deviation of ClF_3 from the ideal-gas laws can be explained by the association of chlorine trifluoride[40] $2ClF_3 \rightleftharpoons (ClF_3)_2$. The heat of this reaction at room temperature has been calculated as 3.3 ± ± 0.5 kcal mole^{-1}.[40] Table 5 shows values of the equilibrium constant

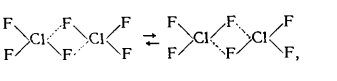
$$K_p = \frac{P^2_{ClF_3}}{P_{(ClF_3)_2}}.$$

Calculated values of K_p for the reverse reaction,

$$(ClF_3)_2 \rightleftharpoons 2ClF_3,$$

are: 0.0372 atm^{-1} at 9.5°, 0.0312 atm^{-1} at 20°, and 0.0283 atm^{-1} at 24.2°. Deductions about the association of ClF_3 have also been drawn from Raman-spectral studies of gaseous and liquid ClF_3.[43,48,49]

A study of the nuclear-magnetic-resonance spectrum[50] has shown that an exchange of fluorine atoms occurs in the ClF_3 molecules. This is evidently due to the presence of dimers,



which are formed through unfilled atomic *d*-orbitals. The exchange of fluorine atoms is possible not only between molecules of ClF_3, but also between ClF_3 molecules, on the one hand, and HF, ClF, or BrF_3 molecules, on the other[51].

TABLE 3. Viscosity of liquid chlorine trifluoride.

Temperature, °C	17.3	17.9	19.4	26.0	32.05	36.3	39.8	48.0
Viscosity, mP	4.48	4.47	4.38	4.07	3.80	3.65	3.52	3.23
Temperature, °C	11.75	15.0	20.0	25.0	30.0	35.0	40.0	50.0
Viscosity, mP	4.78	4.60	4.35	4.12	3.90	3.70	3.51	3.16

TABLE 4. K_p for the reaction $ClF_3 \rightleftharpoons ClF + F_2$.

Temperature, °C	$K_p \times 10^{-4}$ atm
180	0.669
200	0.212
220	0.63
250	2.98
300	24
350	143

TABLE 5. K_p for the reaction $2ClF_3 \rightleftharpoons (ClF_3)_2$.

Temperature, °C	K_p, atm
9.5	26.9
20.0	32.1
24.2	35.4

Studies of the structure of the chlorine trifluoride molecule have been based on determinations of the thermodynamic functions and on optical investigations.

Schafer and Wicke[43] erroneously concluded from Raman-spectral studies that the ClF_3 molecule can be represented by a symmetrical pyramidal model, and Greenwood quotes this in his review[31]. New experimental results show that the symmetrical pyramidal structure for ClF_3 is incorrect. Smith[52,53], on the basis of microwave-spectral studies, considers that the molecule is planar with a C_{2v} axis of symmetry. The moments of inertia obtained[52,53] confirm such a structure and also show that the molecule has a somewhat deformed T-structure with one short (1.598 Å) and two long (1.698 Å) Cl-F bonds. The angle between the different bond types is 87° 29'. The values are 1.621 Å, 1.716 Å, and 86° 59' according to Burbank and Bensey[54]; they put forward the hypothesis that ClF_3 has a layer structure made up of planar triangular molecules, each surrounded by fourteen neighbours. These conclusions are in satisfactory agreement with the presence of a comparatively small dipole moment in ClF_3.

Studies of infra-red absorption spectra, Raman spectra, and nuclear-magnetic-resonance spectra have also confirmed the T-structure for the chlorine trifluoride molecule[50,55]. The deformed T-structure may be considered as being derived from the trigonal bipyramidal molecule[34,56]. The chlorine lies at the centre of the bipyramid and the fluorine atoms are arranged so that two of them are situated at opposite angles of the two pyramide, and the third at one of the angles of the triangle formed by the bases of the pyramids. The two remaining angles of the triangle are occupied by electron pairs of the chlorine atom.

Such a structure satisfactorily explains the tendency of the ClF_3 molecule to form dimers. Muetterties and Phillips[50] believe that the dimer is produced by the formation of bridges from the fluorine atoms between two molecules, the electron pairs from the fluorine atoms occupying 3 d-orbitals of the chlorine atoms. This configuration can be considered to be derived from the octahedral system Sp^3d^2, with two electron pairs occupying two axial positions; the dimer therefore has a planar structure. Because of the increased stability of such a configuration, ClF_3 tends to form dimers.

The same type of structure is also possible for the bromine trifluoride molecule[57]. The halogen fluorides with five atoms of fluorine (BrF_5 and IF_5) form quadrangular bipyramids[58-62], only one angle being occupied by an electron pair. The halogen fluorides with seven fluorine atoms (IF_7) have no lone electron pairs.

3. CHEMICAL PROPERTIES OF CHLORINE TRIFLUORIDE

The distinctive properties of the interhalogen compounds, to which Mendeleev[63] has already drawn attention, are mainly due to the formation of these compounds from atoms of elements belonging to the same Group and sub-group in the Periodic System. The properties of chlorine trifluoride, a compound of two adjacent elements in the same sub-group, clearly reflect this characteristic.

The chemical properties of ClF_3 are to be considered from the point of view of its behaviour as a fluorinating agent. Chlorine trifluoride can react with all the elements with the exception of oxygen, nitrogen, platinum, and the inert gases. According to Ruff and Krug[15], some metals (potassium, molybdenum, tungsten, iron, osmium, iridium) burn in chlorine trifluoride. Sodium, magnesium, aluminium, silver, zinc, and tin react with ClF_3 to form fluorides insoluble in liquid ClF_3, and the metal becomes passive. However, at high temperatures these metals react vigorously with ClF_3.

The metals most resistant to ClF_3 are: mild steel (to 250°), copper (to 400°), and nickel (to 750°)[64]. This is explained by the formation of resistant fluoride films which prevent further attack on the metal.

Chlorine trifluoride acts slowly on dry quartz glass and quartz wool, but in the presence of traces of moisture these are rapidly attacked[16,46,64]. Hydrogen, silicon, phosphorus, arsenic, antimony, sulphur, selenium, and tellurium ignite when acted upon by ClF_3; the composition of the products of most of these reactions has not been established. Many gases (sulphur dioxide, hydrogen sulphide, and ammonia) ignite in ClF_3. ClF_3 reacts with SO_2 to form thionyl tetrafluoride[65,66].

Liquid ClF_3 interacts vigorously with the halogens (Br_2 and I_2) with ignition (and spattering) of the reactants[22] according to the equations

$$2ClF_3 + Br_2 = 2BrF_3 + Cl_2;$$

$$10ClF_3 + 3I_2 = 6IF_5 + 5Cl_2.$$

These reactions have been studied by gradually introducing one reagent into the other with cooling of the mixture and condensation of the products.

Chlorine trifluoride reacts vigorously with water, probably according to the equation[15]

$$3H_2O + 4ClF_3 = 6HF + 3OF_2 + 2Cl_2.$$

Aqueous solutions of alkali decompose ClF_3. Ruff and Krug[15] used this reaction to fix weighed samples in the quantitative analysis of ClF_3. Sulphuric and nitric acids react vigorously with ClF_3.

A study of the isotopic exchange of the fluoride anion between ClF_3 molecules, on the one hand, and molecules of BrF_3 and HF, on the other, has shown that the exchange proceeds according to the reactions

$$HF + ClF_3 \rightleftharpoons ClF_2^+ + HF_2^-;$$

$$BrF_3 + ClF_3 \rightleftharpoons ClF_2^+ + BrF_4^-.$$

The possibility of the formation of an intermediate complex is not excluded. Exchange between gaseous HF and ClF_3 proceeds through the formation of an intermediate complex of composition $ClF_3 . HF$.[67] However, this compound has not been detected in a study of the condensed ClF_3–HF system[68,69]. The $ClF_3 . HF$ is very unstable and is probably present in insignificant quantities in the liquid phase; the presence of a similar complex of bromine trifluoride, $BrF_3 . HF$,[70] has been confirmed. The isotopic exchange of chlorine in ClF_3 has been investigated in studies on the ClF_3–Cl_2 and ClF_3–ClF systems[71].

Gaseous ClF_3 decomposes when it is irradiated with α-particles, the main decomposition products being ClF and fluorine. Calculations show that one molecule of ClF_3 decomposes per 100 eV absorbed by the gas[72].

Organic compounds, as a rule, react with ClF_3 with ignition[42]; for this reason the fluorination of these compounds cannot be controlled. When ClF_3 acts on organic compounds dissolved in fluorinated hydrocarbons[73], carbon tetrachloride[74], or anhydrous hydrogen fluoride, the reaction is relatively mild and can be carried out in the liquid phase; the hydrogen atoms are replaced by fluorine and chlorine. When ClF_3 acts on benzene, toluene or ethylene, addition products of fluorine and chlorine are formed together with some substitution products[50,76,77].

Chlorine trifluoride is widely used to form fluorides by reaction with metals or their compounds. According to Popov and Knudson[21], the oxides of lanthanum and the lanthanides are converted into fluorides by the action of gaseous ClF_3. The degree of fluorination of the oxides and the reaction rates decrease with increasing atomic number; the oxides of the elements from lanthanum to samarium are fluorinated completely to MF_3; Gd_2O_3 is converted to GdF_3 in 80% yield, but the yield of ErF_3 is only 12%. The heavier oxides (Tb to Lu) do not react at all with ClF_3. Yttrium oxide reacts to the extent of only 45% with gaseous ClF_3.

Nikolaev et al.[22,23,24] have synthesised a number of higher fluorides of the transition elements using liquid and gaseous ClF_3. When V_2O_5, WO_3, and MoO_3 react with liquid ClF_3 ignition occurs with atomisation of the reaction products — vanadium pentafluoride, tungsten hexafluoride, and molybdenum hexafluoride. The preparation of these higher fluorides is more conveniently achieved with bromine trifluoride or pentafluoride; with these reagents (for V_2O_5, WO_3, and MoO_3) the reaction is less vigorous. If ClF_3 is used, the gaseous form is more convenient. Gaseous ClF_3 reacts with metallic niobium, tantalum, and molybdenum forming higher fluorides of these metals[23,24]. Quartz apparatus was used in the synthesis of NbF_5, TaF_5, and MoF_6. The reaction starts without external heating; the metal burns in gaseous ClF_3 and the reaction product is distilled into a quartz receiver, cooled with solid carbon dioxide. The reaction can be easily regulated by adjusting the flow of gas. Purification from the excess of fluorine is effected by distillation, by additional fluorination, or by washing the product with liquid hydrogen fluoride at the temperature of dry ice. This synthetic method is applicable in practice to the preparation of a number of higher fluorides.

Hückel[78] prepared HgF_2, AgF_2, CuF_2, TiF_3, PtF_4, and PbF_3 by heating the metals with ClF_3 in an autoclave. When ClF_3 acts on Co_2O_3, cobalt trifluoride is formed[79]. The chlorides of potassium, cobalt, nickel, and silver are converted to the corresponding fluorides by chlorine trifluoride[79,80,81]. The interaction of uranium metal with ClF_3 (both liquid and gaseous) is of great interest; chlorine trifluoride and other known halogen fluorides are used as fluorinating agents in the regeneration of nuclear fuel[25,28,82–86].

The behaviour of ClF_3 as a solvent is best understood from the point of view of the acid-base theory of non-aqueous solvents[13,20,31]. The fluoride ion plays a part similar to that of the proton, addition of a fluoride ion being equivalent to the loss of a proton.

Stein and Vogel[86] considered the fluorination problem from the point of view of the reactivity of uranium metal in different pure halogen fluorides and in mixtures. The experiments were so arranged that it was possible to observe the reaction in both the liquid and the gaseous phases: in all cases uranium was fluorinated with the formation of uranium hexafluoride. The reaction is explosive with gaseous ClF_3. A very large amount of heat (2.2×10^3 kcal kg^{-1})[25] is evolved, which it is practically impossible to remove. Liquid ClF_3 converts uranium metal to UF_6 according to the equation

$$U\ (solid) + 3ClF_3\ (liq.) = UF_6\ (liq.) + 3ClF\ (gas).$$

The use of liquid ClF_3 has several advantages: (1) a high degree of fluorination is achieved at moderate temperatures and pressures; (2) the problem of storing and transporting the fluorinating reagent is simplified; and (3) the problem of heat removal does not arise. However, because ClF_3 is a poor acceptor of fluoride ions in the liquid phase its reactivity to metals is comparatively low (the rate of the reaction between solid uranium and liquid $3ClF_3$ at 30° is $2.5 \times \times 10^{-8}$ moles of uranium per cm^2 of metal surface per second)[72] and is adequate for practical purposes. Anhydrous hydrogen fluoride dissolved in ClF_3 increases the reaction rate[87]. Bernhardt, Barber, and Gustison[72] explain the mechanism of this process in the following way. Pure ClF_3 is slightly ionised:

$$2ClF_3\ (liq.) = ClF_2^+\ (liq.) + ClF_4^-\ (liq.).$$

The instability of the ClF_4^- anion prevents the self-ionisation of ClF_3. The electrical conductivity of ClF_3 at 0°, as already mentioned, is $3 \times 10^{-9} \Omega^{-1} cm^{-1}$. This value is close to that for liquid ammonia, which behaves as an ionising solvent. However, there is a marked difference in the dielectric constants of these compounds (NH_3, 22 at -34°; ClF_3, 4.304 at 25°[34]). The addition of hydrogen fluoride raises the conductivity of the solution because it promotes the formation of the more stable bifluoride anion[72]:

$$ClF_3\ (liq.) + HF\ (liq.) = ClF_3 . HF\ (liq.) = ClF_2^+\ (liq.) + FHF^-\ (liq.).$$

Smith and Pemsler[67] identified the compound $ClF_3 . HF$ in the gas phase; they assumed[72] that the increased activity of ClF_3 when hydrogen fluoride is added is due to the increase in the concentration of the ClF_2^+ ion.

The foregoing explains the importance of a study of the ClF_3–HF system which has been carried out for the solid–liquid equilibrium over a wide range of concentrations (0 to 100% HF) by McGill, Wendolkowski, and Barber[68]. The ClF_3–HF system is of simple type with one eutectic mixture containing 7.5 mole % ClF_3 and having a melting point of -88.8° (Fig.3). The term "molar" is used as equivalent to the term "formula weight", although it is known that hydrogen fluoride must be associated in systems of this type[72]. The authors[68] note the presence of enantiotropy in ClF_3 at -83.1°, significant deviations from the ideal gas laws, and the absence of complex formation in this system.

The liquid–gas equilibrium for the ClF_3–HF system was studied at pressures of 1.5, 2.0, 2.5, 3.0, and 4.0 atm[68,69]. This system forms an azeotropic mixture, containing 67 mole% ClF_3 and 33 mole% HF, whose composition is independent of pressure (Fig. 4). The closeness of this ratio

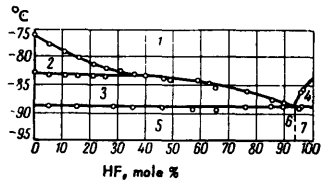


Fig. 3. Solid — liquid equilibrium diagram for the ClF_3—HF system: 1) solution of ClF_3—HF; 2) solid ClF_3 (X-II) + solution; 3) solid ClF_3 (X-I) + solution; 4) solid HF + solution; 5) solid ClF_3 (X-I) + eutectic; 6) eutectic; 7) solid HF + eutectic.

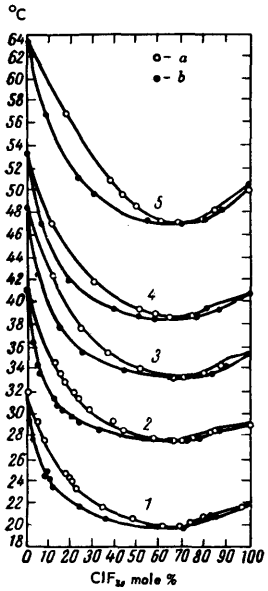


Fig. 4. Liquid — gas equilibrium diagram for the ClF_3 system. Pressure in mm Hg: 1) 1150; 2) 1530; 3) 1900; 4) 2280; 5) 3040. *a*) Vapour; *b*) liquid.

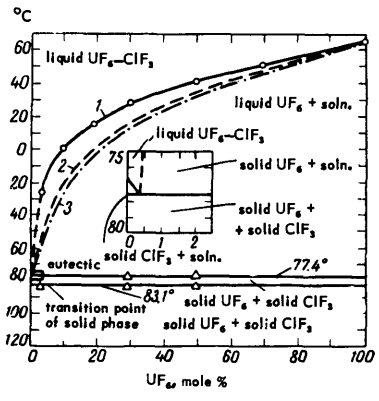


Fig. 5. Solid — liquid equilibrium diagram for the ClF_3 — UF_6 system: 1) experimental curve; 2) theoretical curve; 3) ideal curve.

to the composition of the compound HF . $2ClF_3$ is fortuitous, in spite of the detection of the compound ClF_3 . HF in the gas phase. The melting point for the ClF_3–HF system also gives no indication of the presence of such a compound. At the pressures studied, the boiling point of the azeotrope lies within the range 19.9° to 47.1°.

The solid–liquid and liquid–gas equilibria for the ClF_3–UF_6 system have been studied by Wendolkowski and Barber [88], by Bernhardt, Davis, and McGill [35], and by Ellis and Johnson [89]. The system is simple with a eutectic mixture containing 0.4 mole% of UF_6 and having m.p. -77.4° (Fig. 5). The system shows no compound formation. The liquid–gas equilibrium for the UF_6–ClF_3 system has been studied at the following pressures: 1.5, 2.0, 2.5, and 3.0 atm (Fig. 6). The system does not form compounds of UF_6 and ClF_3 even at higher pressures and there are no azeotropic mixtures. At 67° the components of the system are completely miscible, but at 75° a region of limited miscibility appears within the limit 0.3 to 0.5 mole% UF_6.

Examination of the ClF_3–UF_6 system (liquid–gas) shows that at pressures above 2.5 atm the ClF_3 can be completely separated by fractional distillation from uranium hexafluoride without precipitation of the latter as solid [72,90]; fractional distillation at pressures lower than 2.5 atm is complicated by the formation of solid UF_6.

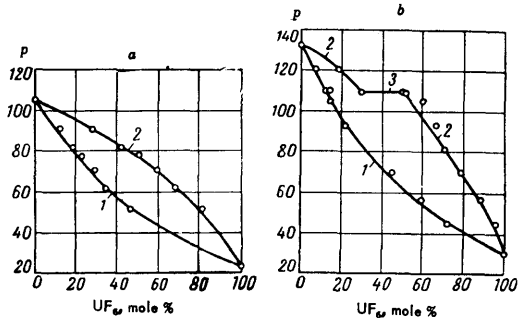


Fig. 6. Liquid — gas equilibrium diagrams for the ClF_3 — UF_6 system: 1) vapour; 2) liquid. *a*) At 67°; *b*) at 75°.

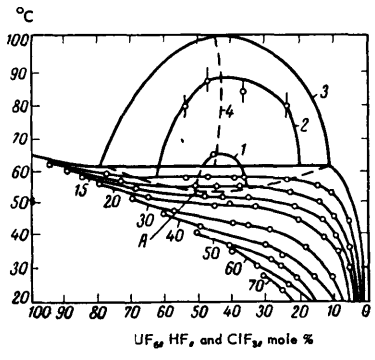


Fig. 7. Solid — liquid — gas equilibrium diagram for the UF_6 — ClF_3 — HF system: 1) 10.0 mole % ClF_3; 2) 5.0 mole % ClF_3; 3) 0.0 mole % ClF_3; A - ternary singular point.

The ternary UF_6–ClF_3–HF system [36,91] (Fig. 7) has been completely studied by way of the systems ClF_3–HF, [68,69] ClF_3–UF_6, [35,88,89] and UF_6–HF. [92,93] The solid–liquid and liquid–gas equilibria were studied over the range -100° to +100°. The UF_6–ClF_3–HF ternary system is of simple type with one eutectic melting at -91°; its composition is 19.5 mole% ClF_3, 80.5 mole% HF, and less than 0.2 mole% UF_6. There is a region of limited miscibility for two liquids saturated with uranium hexafluoride below 53°: at this temperature (composition 13 mole% ClF_3, 38 mole% HF, and 49 mole% UF_6) the two partly miscible liquids become completely miscible. The main features of the liquid–gas equilibrium for the UF_6–ClF_3–HF system [35,72,91,93] were deduced from a study of the three constituent binary systems. The system has no azeotrope, although one is possible for the composition 67 mole% ClF_3 and 33 mole % HF in the UF_6–HF binary system.

The material considered here exhausts the literature data on the systems based on chlorine trifluoride; these are in fact limited entirely to systems that contain uranium hexafluoride and hydrogen fluoride as components. There are no similar studies for systems containing other higher fluorides; the study of these would undoubtedly be of great theoretical and practical interest.

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TERNARY INTERMETALLIC COMPOUNDS

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INTRODUCTION

A large number of binary intermetallic compounds have now been investigated. The scientific classification of such compounds has been based on Kurnakov's[1] treatment of berthollides and daltonides, and this also enables their precise position among binary metallic phases to be defined. The classification of binary intermetallic compounds according to the types of crystal lattices which they form has been dealt with in several monographs[2-4].

Recent reviews have analysed the general features of the structure, formation, and properties of particular groups of binary intermetallic compounds, and have clarified their role in industrial alloys and the possibilities of their practical utilisation. Data on binary metallic compounds have enabled binary equilibrium diagrams to be studied more completely and more thoroughly.

Three-component systems have received much less attention. Various phases, containing from one to three elements, can be formed in such systems; they are for the most part ternary metallic phases, since the pure components of ternary systems, as well as the binary metallic compounds which are often formed in these systems, are always able to dissolve the components present in excess, to some extent, forming ordinary and "metallide" solid solutions respectively.

The present author[5] has worked out a classification of ternary metallic phases based on a comparison of the nature and extent of the homogeneous regions of the ternary equilibrium diagram. Four of the eight types of ternary metallic phases, including ternary solid solutions based on one of the components of the system, cannot be included among intermetallic compounds.

Ternary phases which are metallide solid solutions of limited solubility are similar in structure and properties to

the binary intermetallic compounds on which they are based. Since, as was noted above, a great deal of work has been done on the investigation of binary intermetallic compounds, ternary phases of this type will not be examined here either.

The most interesting are the ternary phases which are represented on the ternary equilibrium diagrams by completely bounded regions of homogeneity, degenerating into points in the absence of ability to dissolve the excess of the components. These phases, usually distinguished by their own types of crystal lattices and their own special properties, represent independent chemical individuals in Kurnakov's sense, and should be termed "ternary intermetallic compounds".

Phases of this type form the main subject of the present paper.

Special note should be made of ternary phases formed by continuous solid solutions between two binary intermetallic compounds. Although these phases represent a particular case of metallide solid solutions, in several instances, especially at or near equimolar concentrations, they develop superlattice lines on the X-ray diffraction patterns and exhibit special properties, differing from those calculated on the basis of additivity, and therefore represent independent phases of the nature of ternary compounds. Such phases will also be discussed further together with typical ternary intermetallic compounds.

1. GENERAL FEATURES OF TERNARY INTERMETALLIC COMPOUNDS

Like the binary compounds, ternary metallic compounds can be formed in alloys as a result of the primary crystallisation, a peritectic transition, separation from solid solutions, or conversion of solid solutions into Kurnakov compounds. The stability of ternary compounds depends greatly on composition, generally increasing with increasing difference in chemical character between the component elements. Both the daltonide and berthollide type of phase is found among typical ternary intermetallic compounds.

An example of a daltonide is the compound $S(Al_2CuMg)$, which has been studied in detail (e.g. refs. 6 and 7). A berthollide character is shown by the ternary compounds T(Al, Cu, Mg)[6] and T(Al, Mg, Zn)[8]. One paper has been particularly concerned with the investigation of ternary berthollides[9].

The main factors governing the composition and crystal structure of ternary metallic compounds are the chemical nature of the component elements, the concentration of valency electrons, and the relative sizes of the atoms (ions). These factors will be examined in greater detail below.

The present author[10] was the first to classify data on the crystal lattices of ternary metallic compounds, describing in all about 250 compounds with an indication of their structural types. Some general rules linking the crystal structure of ternary metallic compounds with concentration of valency electrons and atomic radii have been discussed[11].

Analysis of existing data shows that the majority of ternary metallic compounds crystallise in close packed lattices with high coordination numbers characteristic of pure metals and binary intermetallic compounds. The most widespread among them are lattices with a high degree of symmetry, the cubic and hexagonal lattices.

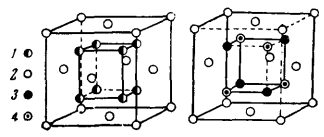


Fig. 1. Crystal lattices of LiMgN and LiZnN[12]: 1) $\frac{1}{2}$Mg + $\frac{1}{2}$Li; 2) N; 3) Zn; 4) Li.

Groups of isomorphous ternary metallic compounds exist, containing different elements from the same or neighbouring Groups of the Periodic System. This indicates the importance of the chemical nature of the elements composing the ternary compound. Some typical examples of such crystal-chemical analogues are examined below.

The character of the crystal lattices of similar ternary metallic compounds depends also on the chemical properties of their component elements. For example, comparison of the lattices of the ternary compounds LiMgN and LiZnN (Fig. 1) shows that they differ only in the distribution of the metal atoms, which is random in the former case (Mg and Li) and ordered in the latter (Li and Zn atoms). This may be explained by the fact that lithium and magnesium differ less in chemical character than do lithium and zinc.

When there is a continuous transition between two ternary compounds, the rearrangement of the crystal lattice is closely associated with a change in the nature of the chemical bond. Thus, in passing from NiMnSb to Ni_2MnSb[13] the lattice changes from the CaF_2 type to the Heusler close packed type (Fig. 2). This is accompanied by a strengthening of the metallic bond, which is confirmed by a corresponding change in magnetic properties and an increase in ductility. Binary and ternary metallic compounds, possessing similar chemical formulae and differing only in chemically analogous elements, often have the same crystal lattices. Typical examples are the pairs of compounds Co_2Al_5 and Fe_2NiAl_{10}, and Co_2Al_9 and $FeNiAl_9$; the members of each pair have very similar X-ray diffraction patterns[14].

Recently increased attention has been paid to research on the crystal structures of ternary intermetallic compounds. Reference must be made to Schubert's work[15] on the application of his theory of the spatial correlation of

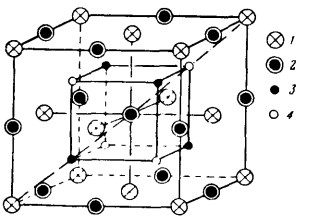


Fig. 2. Crystal lattices of NiMnSb and Ni_2MnSb[13]. Positions of atoms: for NiMnSb: 1) Ni; 2) Sb; 3) Mn; for Ni_2MnSb: O_h^5 type: 1) and 2) Ni; 3) Mn; 4) Sb; T_d^2 type: 1) and 3) Ni; 2) Mn; 4) Sb.

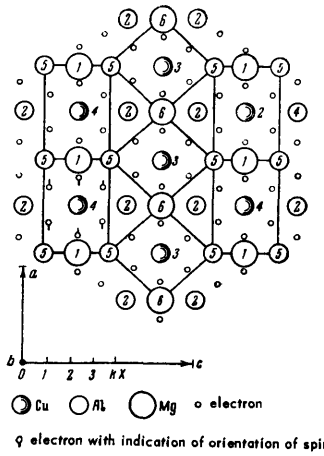


Fig. 3. Crystal lattice of $CuMgAl_2$ [15]. The distribution of atoms and electrons is shown (projection on b axis). The numerals indicate the heights at which atoms are located in multiples of b [14].

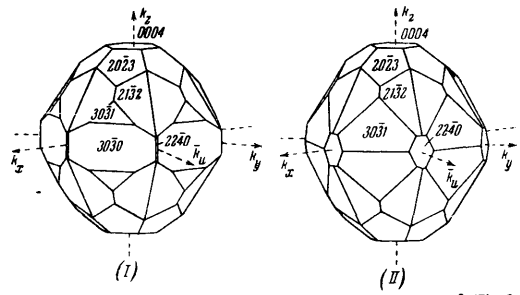


Fig. 4. First Brillouin zones for the structure of (I) the ternary intermetallic compound $MnSiAl_9$ and (II) the binary compound Co_2Al_5 [16].

electrons to explain the lattice structure of ternary compounds. Fig.3 is a diagram of such a model for the $S(Al_2CuMg)$ phase with an indication of the three-dimensional distribution of atoms and electrons.

The arrangement of the atoms has been established exactly, and the Brillouin zones have been constructed, for several ternary metallic compounds possessing complex crystal structures. Comparison of the three-dimensional models of the Brillouin zones for analogous binary and ternary compounds frequently shows a great similarity (see, for example, the models for the compounds Mn_3SiAl_9 and Co_2Al_5 [16] in Fig. 4).

The brief review of ternary metallic compounds given below shows that their composition and structure depend primarily on the chemical nature of the component elements, corresponding to the positions of the latter in the Periodic System. Among them are encountered all the types characteristic of binary compounds. This shows that binary and ternary intermetallic compounds have essentially the same nature.

2. TERNARY KURNAKOV PHASES

The literature hardly mentions the formation of ternary intermetallic compounds by transformations in ternary solid solutions. Reference can be made only to the work of Nemilov and Rudnitskii [17], which demonstrated the formation of a ternary intermetallic compound $CuFePt_2$ at ~1200° as a result of a transformation in a copper–platinum–iron solid solution (Fig. 5). But several investigators have established the influence of a third component on the conditions of formation of binary Kurnakov compounds. For example, the effect of Zn, Ni, Cd, Ti, Mg, Al, Mn, and Ag on the formation of the compounds AuCu and $AuCu_3$ has been ascertained [18–21]. Some of these elements (Zn, Ni, Mn, Ag) lower the temperature of formation of the binary compounds considerably, whereas the others have little effect in this respect. The effect becomes more marked as the quantity of the third element dissolved in the binary compounds is increased.

Extremely interesting and original methods of investigating the chemical bonds in solid solutions have been worked out by Grum-Grzhimailo and tested by him on a large number of experimental results [22–27]. To detect electron bonds between atoms, showing the characteristics of chemical interaction, he used methods based on the measurement of galvano-magnetic effects, the Hall effect, and values of the residual electrical resistivity.

In a study of solid solutions in the Fe–Cr, Fe–Co, Co–Ni, Cu–Ni, etc. systems, characteristic inflections, corresponding to intermetallic compounds of definite composition, were observed on the curves. These investigations

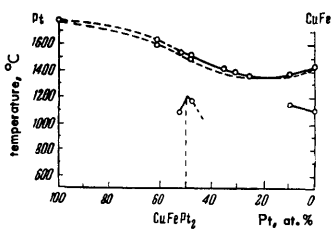


Fig. 5. Equilibrium diagram for Pt – CuFe alloys [17]; formation of the ternary intermetallic Kurnakov compound $CuFePt_2$ is shown.

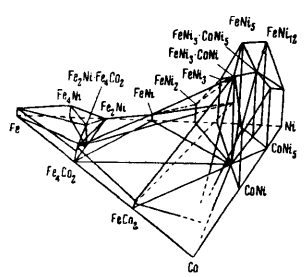


Fig. 6. Intermetallic compounds in the Fe – Co – Ni system [25].

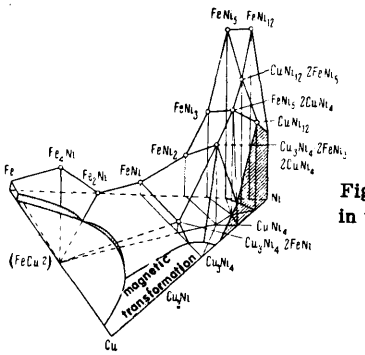


Fig. 7. Intermetallic compounds in the Cu – Fe – Ni system [25].

clearly confirm that a change occurs in the nature of the chemical bonds at concentrations corresponding to the composition of chemical compounds. Application of these methods enabled Grum-Grzhimailo to discover several new, and in particular some ternary, intermetallic compounds. For example, ternary compounds of the composition $Fe_2Ni \cdot Fe_4Co_2$, $FeNi_3 \cdot CoNi$, and $FeNi_5 \cdot CoNi_5$ were detected in the Fe–Co–Ni system (Fig. 6). Several ternary compounds were also found in the Cu–Fe–Ni system (Fig. 7).

The so-called σ- and μ-phases should be classed as Kurnakov phases. The isomorphism of the σ-phases and their related chemical nature suggest that they may form a continuous series of solid solutions. This has been demonstrated, for example, with the FeCr–FeV system [28], in which complete miscibility exists both below and above the temperature range in which the σ-phases are formed (Fig. 8).

Analogous solubility relationships exist for the interaction of μ-phases. For example, it has been confirmed [29] that the isomorphous phases $\mu(Fe_7Mo_6)$ and $\mu(Co_7Mo_6)$ give continuous solid solutions (Fig. 9).

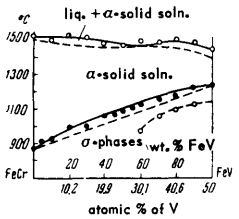


Fig. 8. Continuous solid solutions between the compounds FeCr and FeV (σ-phases)[23]: ○ arrests on the cooling curve; ● arrests on the heating curve.

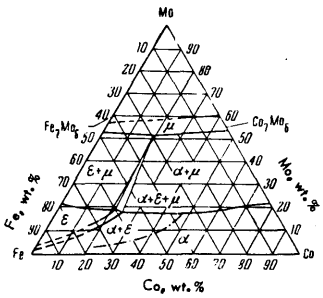


Fig. 9. Continuous solid solutions between the compounds μ (Co_7Mo_6) and μ (Fe_7Mo_6) at 1200° in the Fe – Co – Mo ternary diagram [29].

In several solid solutions of this kind ternary phases are sometimes formed with maximum or minimum values of various properties. In such phases the strength of the chemical bond between the interacting elements undoubtedly changes, and this serves as a criterion of the formation of association complexes, closely similar to typical ternary compounds.

3. TERNARY INTERMETALLIC COMPOUNDS OF NORMAL VALENCY

A large group of ternary compounds containing elements of Groups I and V of the Periodic System have now been studied, several examples being given in Table 1. The component elements of these compounds exhibit valencies corresponding to their positions in the Periodic System. Investigation of analogous compounds of this type shows that their structure and properties vary regularly with change in their chemical composition.

TABLE 1. Ternary valency compounds.

Analogues differing in elements of Group V		Analogues differing in elements of Groups II–IV	
compound	reference	compound	reference
LiMgN	12	LiMgP	30
LiMgP	30	LiZnP	30
LiMgAs	31	Li_3AlP_3	32
LiMgSb	31	Li_3GaP_3	33
LiMgBi	31	Li_5SiP_2	33
		Li_5TiP_2	33
		Li_5GeP_2	33

For example, compounds containing non-metals — LiMgN, Li_3AlP_2, Li_3AlAs_2, AgMgAs, etc. — have a well defined salt-like character, which is confirmed for the majority of them by high melting points, ready hydrolysability, low electrical conductivity, and other properties characteristic of compounds having an ionic bond [32]. On the other hand, analogous compounds formed solely from metals — CuMgBi, CuCdSb, etc. — exhibit more clearly metallic properties and the metallic bond predominates.

A detailed analysis [30,34,35] of the crystal structures confirms this difference in properties and nature of the interatomic bond.

4. ELECTRONIC TERNARY INTERMETALLIC COMPOUNDS

Very few electronic ternary intermetallic compounds satisfy Hume-Rothery's rules if the concentration of valency electrons is calculated in the usual way, and in particular if elements of Group VIII are given zero valency. For example, $MgSnNi_2$ [36] and $CuAuZn_2$ [37] have an electron concentration (electron : atomic ratio) of 1.5 and crystallise in

TABLE 2. Number of electron vacancies in certain metals (from magnetic measurements).

Element	Ni	Co	Fe	Mn	Cr
Number of electrons per atom in "atomic" orbitals	0.61	1.71	2.66	3.66	4.66

TABLE 3. Concentration of valency electrons and crystal lattices of some ternary intermetallic compounds.

No.	Group	Concentration of valency electrons, electrons per atom	Ternary compound	Crystal lattice	Reference
1		1.85	$T(Cu_2Al_{20}Mn_8)$	orthorhombic	41
2		1.85	$T(ZnAl_{24}Mn_5)$	orthorhombic	41
3	I	1.85	$\alpha(Al_3SiCr)$	cubic	39
4		1.85	$\beta(Al_9SiMn_2)$	hexagonal	16
5		1.85	$T(Al_{60}Mn_{11}Ni_4)$	orthorhombic	41
6		2.04	$N(Cu_2Al_7Fe)$	tetragonal	42
7		2.04	$\tau(Cu_3Al_6Ni)$	cubic	43
8	II	2.04	$T(Cu_5Al_{13}Co_2)$	—	44
9		2.04	$\alpha(Al_{12}SiFe_3)$	cubic	42
10		2.04	$\alpha(Al_{10}SiMn_2)$	cubic	42
11		2.37	$E(Mg_3Al_{25}Cr_2)$	cubic	45
12	III	2.37	$T(\sim Mg_2Al_{10}Mn)$	—	46
13		2.37	$\beta(Al_{1.5}SiFe)$	monoclinic	42
14		2.37	$\pi(Al_9FeNi)$	monoclinic	14

the β-brass structure. If the valency of manganese is taken as unity[11], such compounds as Cu_2MnAl, Cu_2MnIn, Co_2MnSn, Ni_2MnSn, etc. also can be included among electronic β-phases.

The majority of other electronic ternary compounds do not obey Hume-Rothery's rule. In order to explain their structure, Raynor and his collaborators[38,39] used Pauling's theory[40], based on the hypothesis of a "negative" valency for the transition metals with unfilled d-levels. According to this theory, when aluminium and silicon form ternary compounds with the transition metals of the Fourth Period, the Al and the Si give up their valency electrons to the common electron atmosphere, whereas the transition metals capture some of these electrons in order to complete their d-levels. The number of electrons which are thus captured depends on the position of the element in the Periodic System, and can be calculated from the magnetic properties of these elements. Thus the transition metals should not be assigned a zero valency, as in the binary Hume-Rothery phases, but some negative valency; according to Pauling this is equal to the number of electrons in the so-called "atomic" orbitals (Table 2).

TABLE 4. Number of electron vacancies in certain metals[38].

Element	Ni	Co	Fe	Mn	Cr
Number of electrons per atom in "atomic" orbitals	0	1	2	3	4

TABLE 5. Number of electron vacancies in certain metals.[28]

Element	Ni	Co	Fe	Mn	Cr
Number of electrons per atom in "atomic" orbitals	1.6	1.71	2.2	3.2	4.66

If the electron concentrations are calculated from these values for various ternary compounds, the latter can be divided into groups having the same ratios (Table 3 and Fig. 10).

In group I, compounds 1, 2, and 5 are isomorphous; they all contain 80 at.% of aluminium.

In group II, compounds 9 and 10 are isomorphous, and together form a continuous series of solid solutions[38].

In group III, compounds 13 and 14 have similar monoclinic lattices; it is interesting that the electron : atom ratio corresponding to this group is also reached in the isomorphous saturated solutions of silicon or nickel in the binary compound Co_2Al_9; Raynor and Pfeil[47] consider that this ratio is in general a limiting value for ternary intermetallic compounds.

It is possible to calculate the electron concentration by a different method[38], on the hypothesis that the transition metals take up an integral number of electrons per atom (Table 4).

However, results obtained by this method agree less well with the shape and size of the Brillouin zones, and do not give as good agreement with the values for the electron concentration in some solid solutions based on binary intermetallic compounds.

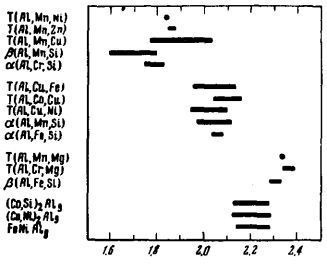


Fig. 10. Concentration of valency electrons in ternary compounds containing aluminium and transition metals [38].

The values of the number of electron vacancies adopted for the transition metals in these calculations are not actually encountered. Thus, a paper[29] on solid solutions between σ- and μ-phases in some ternary systems considers it expedient to assign to the transition metals the numbers of electron vacancies indicated in Table 5. In this case, for example, for solid solutions between μ-phases, the concentration of valency electrons remains constant at 2.95–3.24 electrons per atom.

The examples which have been quoted show a certain artificiality in the calculation of electron concentrations on

the basis of the theory of electron vacancies, which appears in a tendency to round off the values of this quantity for the separate groups of ternary metallic phases. Further, the data in Table 3 show that the relations between electron concentration and crystal structure, found by Hume-Rothery for binary intermetallic compounds, are not exhibited by ternary compounds, apart from rare exceptions. Thus the results of the study of ternary compounds of electronic type do not yet provide a satisfactory explanation of their structure. Only a more thorough investigation of the conditions of chemical interaction between the elements in the formation of these compounds will enable their nature to be ascertained and their inherent properties to be explained.

A much clearer idea has been obtained of the structure of ternary electronic phases which are solid solutions between binary electronic compounds. In the majority of cases, binary compounds which are Hume-Rothery phases, possessing the same electron concentration and the same types of crystal lattices, form continuous series of solid solutions; a few examples are given in Table 6*.

The formation of such continuous solid solutions is subject in the majority of cases to the conditions formulated by Kornilov[56]. In this case binary compounds which are chemically similar and are composed of analogous elements generally form continuous solid solutions characterised by a constant value of the electron concentration.

5. TERNARY LAVES PHASES

Among ternary intermetallic compounds phases have been found with the homeotectic structures $MgCu_2-MgNi_2-MgZn_2$, with ratios of atomic radii characteristic of binary Laves phases.

A systematic and detailed analysis of the crystalline structure of these phases, which are distinguished by high coordination numbers, has been given by Kripyakevich[59]. Another paper[11] has discussed several ternary Laves phases and has stressed their wide distribution.

Table 7 lists a few examples[60].

For these compounds R_A/R_B is on the average 1.206, which differs little from the ideal ratio (1.225).

The chemical similarity of compounds composed of analogous elements is noteworthy. This shows that the chemical nature of the elements composing a given group of compounds is important, in addition to the volume factor.

Binary Laves phases seldom form continuous series of solid solutions among themselves. Their interaction is typified rather by cases of successive transition from an $MgCu_2$ structure through $MgNi_2$ to $MgZn_2$, as observed in several ternary systems[61-65]. It is possible that the intermediate phases formed in this process may be ternary intermetallic compounds.

6. TERNARY NICKEL ARSENIDE PHASES

As yet, few ternary metallic compounds have been found to have the NiAs structure. Examples are the compound BeSiZr[66], and a few compounds containing germanium (MnFeGe, MnCoGe, MnNiGe, FeCoGe, FeNiGe), and some others, of which a systematic account has been given[67].

* More complete data have been given previously[5].

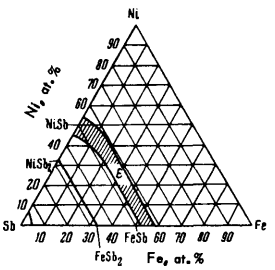


Fig. 11. Continuous metallide solutions in the Sb — Fe — Ni system[69].

However, many ternary phases which are continuous solid solutions of two binary compounds are known, several examples being given in Table 8. The range of solid solution between FeSb and NiSb is shown in Fig. 11[69]. This system is an interesting example of the formation of a continuous series of solid solutions between a daltonide (NiSb) and a berthollide (FeSb).

Chemically these phases are very similar, since they are formed from analogous elements of Group V and VIII.

TABLE 6. Continuous solid solutions between binary electronic compounds.

β-Brass type, 3/2 *		γ-Brass type, 21/13 *		ε-Phase type, 7/4 *	
system	reference	system	reference	system	reference
CuZn — AgZn	48	Cu_5Zn_8—Ag_5Zn_8	53	$CuZn_3$ — $AgZn_3$	57
AgMg — AgCd	48	Ag_5Cd_8—Ag_5Zn_8	48	$CuZn_3$ — $MnZn_7$	57
AgMg — AgZn	49	Cu_5Zn_8—Cu_9Al_4	54	$AgZn_3$ — Ag_5Al_3	58
AgCd — AgZn	48	Cu_5Zn_8—γ(Cu, Ga)	55	$AgZn_3$ — $MnZn_7$	57
AlFe — AlCo	50	Cu_5Zn_8—$Cu_{31}Sn_8$	56		
AlFe — AlNi	51				
AlCo — AlNi	52				

* Concentration of valency electrons, electrons/atom.

TABLE 7. Ternary Laves phases.

Crystal structure	Composition	Ratio of radii R_A/R_B	Crystal structure	Composition	Ratio of radii R_A/R_B
$MgCu_2$	CuCdZn	1.15	$MgZn_2$	$Cu_{1.5}MgSi_{0.5}$	1.24
				CuMgAl	1.18
	$Ag_{0.3}MgZn_{1.2}$	1.14		$Ag_{0.9}MgAl_{1.1}$	1.12
					1.37
	$MgZn_{1.3}Co_{0.7}$	1.21	$MgNi_2$	CuMgZn	1.21
				$Cu_{1.4}MgSi_{0.6}$	1.23
	MgNiZn	1.23		CuMgAl	1.18
				$Ag_{0.4}MgZn_{1.6}$	1.16
	$MgSi_{0.2}Ni_{1.8}$	1.30			

TABLE 8. Continuous solid solutions between binary compounds of the nickel arsenide type.

System	Reference	System	Reference
FeSb — CoSb	69	CoSb — NiSb	48
FeSb — NiSb	69	NiAs — NiSb	71
CoAs — NiAs	70	NiSb — NiBi	48

In addition, they provide a clear example of the rules established earlier[56], governing the formation of continuous metallide solid solutions.

7. TERNARY INTERSTITIAL PHASES

Borides. The formation of ternary compounds containing boron has been noted[72,73], and the compositions of the ternary borides which have been obtained are indicated in Table 9.

Comparison of the formulae for the ternary borides shows that chemically they are very similar, since within each of the columns in Table 9 they differ only in the analogous elements of Group VIII of the Periodic System.

TABLE 9. Ternary compounds containing boron.

Composition	Reference	Composition	Reference
Mo_2FeB_2	72	Mo_2FeB_4	72
Mo_2CoB_2	72	Mo_2CoB_4	72
Mo_2NiB_2	72	Mo_2NiB_4	72
		Cr_2NiB_4	73

TABLE 10. Continuous solid solutions between borides.

System	Reference	System	Reference	System	Reference
$TiB_2 - ZrB_2$	74	$TiB_2 - CrB_2$	75	$CrB_2 - MoB_2$	78
$TiB_2 - HfB_2$	75	$TiB_2 - MoB_2$	75	$CrB - MoB$	78
$ZrB_2 - HfB_2$	75	$ZrB_2 - MoB_2$	75		
$TiB_2 - VB_2$	75			$MnB_2 - FeB_2$	79
$TiB_2 - NbB_2$	76	$VB_2 - CrB_2$	75	$MnB_2 - CoB_2$	79
$TiB_2 - TaB_2$	75	$NbB_2 - CrB_2$	75		
$ZrB_2 - NbB_2$	75	$TaB_2 - CrB_2$	75	$FeB_2 - CoB_2$	79
$ZrB_2 - TaB_2$	77				

TABLE 11. Ternary compounds containing carbon.

Composition	Reference	Composition	Reference	Composition	Reference
Fe_2Mo_2C	80	Fe_3Mo_3C	85	Fe_4Mo_4C	80
Fe_2W_2C	81	Fe_3W_3C	81	Fe_4W_4C	88
Co_2W_2C	82	Co_3Mo_3C	86		
		Co_3W_3C	87	Fe_6Mo_6C	80
Fe_2Mo_4C	83	Ni_3Mo_3C	83	Fe_6W_6C	81
Co_2Mo_4C	84	Ni_3W_3C	85	Co_6W_6C	84
Co_2W_4C	83			Ni_6W_6C	89
Ni_2Mo_4C	83	Mn_3Mo_3C	83		
		Mn_3W_3C	83	$Fe_{21}Mo_2C_6$	90
				$Fe_{21}W_2C_6$	90

The formation of continuous solid solutions between binary borides (Table 10) has been established in several cases. Analysis of these systems shows that (1) the formation of continuous solid solutions follows the main rules[56]; (2) in many cases continuous solid solutions are formed between binary compounds composed of analogous elements*; (3) in all known cases (with the exception of three systems containing elements of Groups IV and VI) continuous solid solutions are formed between binary borides containing transition metals belonging either to the same Group or to adjacent Groups of the Periodic System.

These data indicate the closely similar chemical character and common structure within the separate groups of boron-containing solid solutions.

Carbides. Ternary compounds containing carbon form a particularly clear example of chemical analogy. Several groups of such compounds exist containing different analogous elements, and possessing the same molecular composition and isomorphous crystal lattices (Table 11).

The carbides which have been studied contain predominantly elements of Groups VI and VIII. Many of them can dissolve the excess of the components, and form homogeneous regions on the ternary diagrams. They all form interstitial phases.

Several ternary phases containing carbon represent solid solutions between isomorphous carbides (Table 12).

Here, too, chemical analogy is well developed. The systems included in Table 12 are composed of phases containing elements of either Group IV or Group V.

Silicides. Among ternary silicides the most thoroughly studied are ternary compounds containing aluminium or

TABLE 12. Continuous solid solutions between carbides.

System	Reference	System	Reference
TiC — VC	91	VC — NbC	91
TiC — NbC	92	VC — TaC	91
TiC — TaC	92	NbC — TaC	91
ZrC — NbC	92		
ZrC — TaC	92		
HfC — TaC	93		

TABLE 13. Ternary compounds containing silicon.

Compound	Reference	Compound	Reference
$NaAlSi_4$	94	TiFeSi	98
$MgAl_6Si$	95	$V_5Fe_4Si_4$	99
$\alpha(CrAl_5Si)$	39		
β(Cr, Al, Si)	39	$MoNi_4Si_2$	100
$\alpha(Mn_3Al_{21}Si_5)$	39	Mo_2Ni_3Si	100
$\beta(Mn_3Al_9Si)$	96	WFeSi	101
$\alpha(Fe_{1.5}Al_6Si)$	97	W_2FeSi	101
$\beta(FeAl_{4.5}Si)$	97	$MnCo_2Si$	102
$\gamma(Fe_{0.5}Al_{1.5}Si)$	97		

* In Table 10 such systems are grouped separately.

TABLE 14. Continuous solid solutions between silicides.

System	Reference	System	Reference
V_3Si—Cr_3Si	103	Ti_5Si_3—Zr_5Si_3	104
V_3Si—Mo_3Si	103	VSi_2—$NbSi_2$	105
		Cr_3Si—Mo_3Si	106
		$MoSi_2$—WSi_2	107

TABLE 15. Ternary compounds containing nitrogen.

Compound	Reference	Compound	Reference
$Ti_{0.7}Co_{0.3}N$	68	$Ta_2FeN_{2.5}$	108
$Ti_{0.7}Ni_{0.3}N$	68	$Ta_2CoN_{2.5}$	108
$Mo_{0.8}Co_{0.2}N$	68	$Ta_2NiN_{2.5}$	108
$Mo_{0.8}Ni_{0.2}N$	68		

TABLE 16. Continuous solid solutions between nitrides.

System	Reference	System	Reference
TiN—ZrN	109	TiN—VN	109
		TiN—NbN	109
ZrN—HfN	109	ZrN — NbN	109
		HfN—NbN(?)	109

elements of Group VIII. Several examples are given in Table 13. Ternary silicides which are electronic compounds have been discussed above (Table 3).

The limited experimental data available on complex silicides do not permit any generalisations to be made. Only a few representatives (e.g. Mn_3SiAl_9, see above) have been studied in detail. A few ternary silicides represent continuous solid solutions between binary compounds (Table 14).

The first two systems in Table 14 are chemically analogous. The remaining systems contain analogous elements of Groups IV—VI and agree well with the rule governing the formation of continuous solid solutions[48].

Nitrides. Ternary compounds of non-valency type containing nitrogen were discovered relatively recently. Several of them, summarised in Table 15, display a well defined similarity of chemical structure. Comparison of the continuous solid solutions formed by nitrides (Table 16) also shows the closely similar chemical nature of ternary phases containing nitrogen.

Analysis of the above data shows that, in all known groups of typical ternary intermetallic compounds and ternary phases formed by continuous metallide solid solutions of two binary compounds, the chemical factor has a strong influence, expressing itself in the chemical and structural similarity between ternary phases of a given group. The role of the chemical factor is predominant also in the formation of ternary phases of classes other than ternary compounds[11], e.g. metallic solid solutions of limited solubility or ternary solid solutions based on one of the components of the ternary system. In many cases this enables us to predict the formation of certain ternary phases in systems not yet investigated, and thus greatly facilitates the construction of the equilibrium diagrams for such systems.

8. PROPERTIES AND PRACTICAL APPLICATION OF TERNARY METALLIC COMPOUNDS

Very little work has been done on the properties of ternary metallic compounds. But even the existing experimental data enable a relation to be established between the properties and the chemical nature of such compounds.

Table 17 gives the colours of "valency" compounds. It is readily seen that in each triad of compounds with two elements in common the intensity of the colour increases regularly with increase in the atomic number of the third element (Group V).

Numerous investigations on the so-called "Heusler alloys" [111-123] have proved their magnetic properties to be closely linked with the formation of the ternary compounds Cu_2MnAl, Cu_2MnGa, Cu_2MnIn, and Cu_2MnSn. The first three are chemical analogues, and the fourth differs from them only in a single element which is similar in chemical character.

TABLE 17. Colours of some "valency" ternary compounds.

Composition	Colour	Reference	Composition	Colour	Reference	Composition	Colour	Reference
LiMgN	light reddish brown	33	Li_3GaN_2	light grey	110	Li_5GeN_3	yellowish	33
LiMgP	brown	30	Li_3GaP_2	medium brown	33	Li_5GeP_3	brown	33
LiMgAs	—	33	Li_3GaAs_2	blackish brown to black	33	Li_5GeAs_3	greyish black	33
Li_3AlN_2	white to light grey	110	Li_5SiN_3	greyish yellow	33	Li_5TiN_3	yellow	33
Li_3AlP_2	yellowish brown	32	Li_5SiP_3	brown	33	Li_5TiP_3	brown	33
Li_3AlAs_2	reddish brown	32	Li_5SiAs_3	greyish block to block	33	Li_5TiAs_3	block	33

This type of relationship is displayed also in other ternary systems. For example, the ternary compounds Co_2MnGe, Ni_2MnGe, Co_2MnSn, and Ni_2MnSn, which are similar in chemical character and have the same crystal lattices, all show magnetic properties[124]. Chernov and the author[125] have determined the electrode potentials of

TABLE 18. Electrode potentials of some ternary intermetallic compounds containing magnesium or aluminium.

Ternary compound	Electrode potential at 20°, V*	Reference	Ternary compound	Electrode potential at 20°, V*	Reference
MgLiZn	—1.199	—	$Al_9Si_3Mn_4$	—0.557	125
$Mg_5Ca_2Zn_5$	—1.129	—	$Mg_2Al_{12}Cr$	—0.470	125
$Mg_4Zn_3Al_3$	—0.826	125	MgCuZn	—0.459	—
$MgLiAl_2$	—0.689	—	$MgCu_4Sn$	—0.019	—

* The values given represent the steady potentials in 3% NaCl solution relative to the hydrogen electrode.

TABLE 19. Microhardness of some ternary compounds containing magnesium.

No.	Ternary compound	Microhardness at 20° $H_{□}$, kg/mm²	Reference	No.	Ternary compound	Microhardness at 20° $H_{□}$, kg/mm²	Reference
1	MgLiZn	239	—	5	Mg_2Cu_4Sn	445	—
2	$MgLiAl_2$	297	—	6	$Mg_5Ca_2Zn_5$	322	—
3	MgCuZn	381	—	7	$Mg_4Zn_3Al_3$	345	125
4	$MgCuAl_2$	380—400	7	8	$Mg_2Al_{12}Cr$	461	125

several ternary intermetallic compounds containing magnesium or aluminium (Table 18).

Comparison of ternary compounds having two elements in common shows that, in the majority of cases, with increasing difference in chemical properties between each of these two elements and the third element, the potentials become more positive.

Quantitative values have been determined for the microhardness of individual ternary intermetallic compounds[7,125-127]. The present author has determined the microhardness of several ternary compounds containing aluminium and magnesium, of interest as light aircraft alloys. The results of these investigations are set out in Tables 19 and 20.

In the majority of cases the microhardness increases with increasing difference in chemical character between the elements forming the ternary compounds. This type of regularity can be observed on comparing ternary compounds containing two elements in common, e.g. Nos. 1 and 2, 3—5, 6 and 7, and 7 and 8 (Table 19). Also, in this

TABLE 20. Microhardness of some ternary compounds containing aluminium.

No.	Ternary compound	Microhardness at 20° $H_{□}$, kg/mm²	Reference	No.	Ternary compound	Microhardness at 20° $H_{□}$, kg/mm²	Reference
1	Al_2LiMg	297	—	9	T(Al,Cu,Mn)	628	127
2	$Al_3Mg_4Zn_3$	345	125	10	T(Al,Si,Mn)	880	127
3	$Al_2Mg_3Zn_3$	422	127	11	Al_6Cu_3Ni	740	125
4	Al_2CuMg	380—400	7	12	Al_9FeNi	860	125
5	Al_6CuMg_4	414	127	13	Al_9FeNi	987	127
6	$Al_{20}Cu_2Mn_3$	421	125	14	α(Al,Si,Fe)	1097	127
7	$Al_{12}Mg_2Cr$	461	125	15	Al_4Si_2Fe	1147	127
8	T(Al,Si,Mn)	589	125				

TABLE 21. Microhardness at 300° of ternary compounds containing aluminium.*

Ternary compound	Microhardness, kg/mm², after		Ternary compound	Microhardness kg/mm² after	
	30 sec	60 min		30 sec	60 min
$Al_{60}Mn_{11}Ni_4$	307	231	$Al_9Mn_4Si_3$	458	361
$Al_3Mg_4Zn_3$	225	101	Al_6Cu_3Ni	585	316
$Al_{20}Cu_2Mn_3$	404	302	Al_9FeNi	719	414
$Al_{12}CrMg_2$	402	358			

* Load on indenter 50 g.

series of ternary compounds containing magnesium, the hardness is greater when the magnesium is combined with elements which are well removed from it in the Periodic System (Nos. 5—8 have $H_{□}$ = 445 and 461 kg/mm²) in comparison with ternary compounds composed of more closely related elements (Nos. 1—4, and 6 and 7, with a hardness $H_{□}$ = 239—345 kg/mm²).

A similar regularity is in general observed in a group of ternary compounds containing aluminium (Table 20). Thus the hardness of compounds 1—5 in Table 20, which contain only elements of Groups I and II of the Periodic System, apart from aluminium, lies in a comparatively low range ($H_{□}$ = 297—414 kg/mm²); compounds 6—10, containing elements of Groups VI and VII, are harder ($H_{□}$ = = 421—880 kg/mm²); finally the last five compounds (Nos. 11—15 in Table 20), containing elements of Group VIII, have the greatest hardness ($H_{□}$ = 740—1147 kg/mm²).

Thus, the hardness of ternary metallic compounds depends to some extent on the position of the component elements in the Periodic System, increasing with increasing difference between the chemical properties of the elements.

Several papers[125,126,127] have been concerned with the determination of the hardness of ternary metallic compounds at elevated temperatures. The microhardness at 300° of several ternary compounds containing aluminium is shown in Table 21 [125].

At a sufficiently high temperature the majority of intermetallic compounds pass into a plastic condition, becoming easily deformable. This was first demonstrated for binary compounds by Savitskii. He carried out a great amount of experimental work[128-131], published in an extensive monograph[132], which showed the possibility of pressing intermetallic compounds at high temperatures and examined in detail the accompanying changes in structure and properties.

Our experiments on the pressing of ternary intermetallic compounds also show that those which are brittle at ordinary temperatures pass into a plastic condition on heating and can undergo considerable deformation. In particular, it was found that the possibility of deforming certain ternary compounds (e.g. $Ca_2Mg_5Zn_5$) enables us to impart a more favourable structure to them, and to alter the ductility of the alloy as a whole favourably.

In conclusion it must be noted that the experimental data are still insufficient to establish definite quantitative relations between the composition of ternary compounds and their properties. However, the investigations which have been carried out indicate the existence of certain regularities in this respect, determined by the chemical nature of

the elements forming the ternary compound: with increasing difference in chemical properties between the elements, the strength of the chemical bond linking them increases correspondingly, and the resulting ternary compounds become more stable; owing to this, their hardness is increased, their melting points are raised, and their electrode potentials become more noble. In several cases these properties can be successfully exploited to improve the mechanical properties, heat resistance, and corrosion resistance of alloys.

Ternary compounds are encountered in the structure of many alloys of practical importance. In this connection, most work has been done on aluminium alloys[133-142]. Ternary compounds are present in these alloys both in the structurally independent state as eutectics or solid solutions. The properties of ternary compounds and the conditions in which they react with the metal on which the alloy is based, enable the following general principles to be laid down for their practical exploitation:

1. Hardening of solid solutions by dissolving ternary intermetallic compounds in them. The formation of such ternary solid solutions involves more complex interatomic bonds than in binary solid solutions, with greater distortion of the crystal lattice, which makes it stronger.

2. Hardening of alloys by forming structurally free ternary intermetallic compounds in them, distinguished by improved mechanical properties. Several such ternary compounds possess greater hardness than the binary compounds, and therefore the hardening effect may also be more strongly marked. A typical example is the increase in the hardness of tool steels as a result of the formation of ternary carbides of the type Fe_2W_2C, Fe_6W_6C [81,143], Ti_2W_2C [144], etc.

3. Hardening of alloys by ternary compounds containing relatively more of the metal on which the alloy is based than in binary compounds. In this case the influence of alloying elements on the structure and properties of the alloy is considerably greater than in the formation of binary compounds.

Thus Dudzinski et al.[145,146] have shown that the formation of ternary compounds in several aluminium alloys can raise appreciably their normal moduli of elasticity. Pointing out that in isolated cases the modulus of aluminium alloys is increased by ~20%, they note the great and practically important effect of ternary intermetallic compounds on the properties of industrial, and in particular aircraft, alloys.

4. Utilisation of the temperature variation of the solubility of ternary compounds in the main metal to achieve hardening by heat-treatment, consisting in a quenching process followed by ageing. It has been found with several ternary systems that solid solutions may be in equilibrium with various ternary intermetallic compounds; with many alloys which form "metal–ternary intermetallic compound" systems, it has been proved that the solubility of the ternary compound increases on heating. Thus by quenching certain alloys of this type it is possible to obtain supersaturated solid solutions, which can be hardened by subsequent ageing.

The possibility has been noted of using ternary compounds for the age-hardening of aluminium alloys[16,138,147,148]. Special reference must be made to a series of papers by Bagaryatskii[149-152], in which a detailed analysis is given of the role of the ternary phase $S(Al_2CuMg)$ in the ageing of aluminium alloys. The ternary compound T(Al, Mg, Zn)

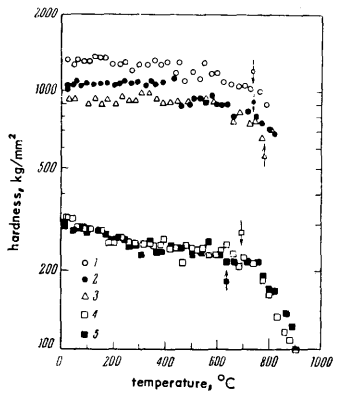


Fig. 12. Effect of temperature on the hardness of some intermetallic compounds and heat-resistant alloys [163]; the arrows indicate 0.6 × m.p.: 1) η_1 — Fe_4Mo_2C; 2) η_2 — Fe_2Mo_4C; 3) Fe_7Mo_6; 4) S-816 alloy; 5) "Jetalloy 1650" alloy.

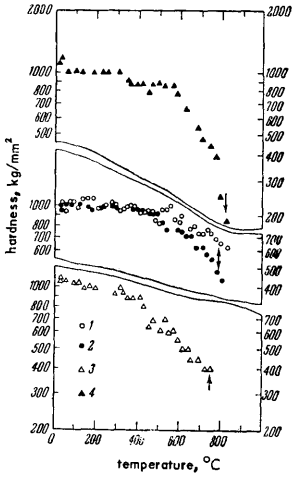


Fig. 13. Effect of temperature on the hardness of some intermetallic compounds [163]; the arrows indicate 0.6 × m.p.: 1) σ - $Fe_{36}Cr_{12}Mo_{10}$; 2) χ - $Fe_{36}Cr_{12}Mo_{10}$; 3) σ - CoCr; 4) σ - FeCr.

has a similar role[153-156]. Our investigations[157-159] of cast and extruded alloys based on aluminium and on magnesium have demonstrated the possibility of hardening these alloys with ternary intermetallic compounds.

5. Improvement of the heat-resistance of alloys containing ternary intermetallic compounds by producing a favourable structure which will as far as possible prevent plastic deformation on heating. As Kornilov[160-162] and others have shown, at certain temperatures such a structure corresponds to saturation of a solid solution. In this case solid solutions which are saturated with ternary intermetallic compounds are formed. In view of the greater complexity of the crystal lattice, ternary solid solutions should possess greater resistance to deformation at high temperatures, as compared to binary solid solutions. The breakdown of

ternary solid solutions with the incipient precipitation of ternary intermetallic compounds, or their separation in a state of dispersion, may also produce an increase in the resistance to plastic deformation on heating, and hence raise the heat-resistance.

The great hardness and thermal stability of several ternary metallic compounds can also be utilised in developing heat-resistant alloys. Some ternary compounds[163] considerably surpass modern heat-resistant alloys (Fig. 12) and binary compounds (Fig. 13) in their hardness at ordinary, and especially at elevated, temperatures.

We have demonstrated the possibility of improving the heat-resistance of aluminium alloys by means of ternary intermetallic compounds[164,165].

6. Improvement in the corrosion resistance of alloys by the introduction and appropriate structural distribution of ternary compounds possessing suitable electrode potentials in given operational environments. A special investigation has been made to determine the effect of ternary intermetallic compounds on the corrosion resistance of pressed aluminium alloys[166].

7. Production of alloys having definite physical properties by utilising the appropriate properties of ternary intermetallic compounds. An example is provided by the work on Heusler alloys already cited[111-123].

8. Employment of ternary intermetallic compounds to impart predetermined technological properties to alloys. Reference must be made to work on the effect of ternary compounds on the modification of Silumins[167-170], on the ductility of cast aluminium alloys[133,171] and of chromium–manganese alloys[172], and also on metal-refining processes for refining metals, e.g. the decarbonisation of uranium[173]. The influence of ternary compounds on the properties of aluminium and magnesium alloys has been discussed in greater detail elsewhere[174].

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CONSTRUCTIONAL PLASTICS, THEIR PRODUCTION AND APPLICATION

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The outstanding success of polymer chemistry has enabled new types of plastic materials to be produced, possessing a remarkable combination of properties, especially great mechanical strength. These plastic materials are being more and more widely employed in the national economy as constructional materials, competing with metals and often replacing them.

1. GLASS-REINFORCED PLASTICS

Among constructional materials a special position is occupied by plastics reinforced with glass. This type covers a group of materials with different physical and mechanical characteristics, technological properties, and fields of application.

Glass-reinforced plastics can be conventionally divided into four main groups according to the type of reinforcement and the technical properties: (1) glass fabrics, (2) oriented glass fibres, (3) plastics based on preformed unoriented glass fibre or mat, and (4) cast or moulded materials incorporating glass fibre.

The problem of using glass-reinforced plastics in different branches of technology covers a complex of questions associated with the production of the glass-fibre reinforcement, the synthesis of binders, the processing and production of the plastic, and the design, manufacture, and application of articles made from it.

The wide use of glass-fibre materials as reinforcing agents is connected with the great mechanical strength of glass fibres, which depends on the chemical composition of glass, the diameter of the fibres, and the technical process by which they have been manufactured.

Glass-reinforced plastics are based mainly on fibres made of an aluminium borosilicate glass containing no alkali, and much more rarely on an alkali glass. The latter contains a large amount of sodium or potassium oxide, and the resulting fibres undergo an irreversible diminution in strength when subject to the action of moisture and temperature. A non-alkali glass fibre is comparatively unaffected by moisture, can be employed without appreciable diminution in strength at temperatures up to 300°–400°, and possesses good electrical insulating properties.

The great merit of fibres based on an alkali-containing glass is the availability and cheapness of the raw materials, and the ease of manufacture of the fibres. Such fibres possess good stability to the action of acids, and therefore with appropriate choice of binder they can be employed in the chemical industry. In this connection, more work must be carried out on the application of glass-fibre fillers based on an alkali glass in the production of plastics and articles made from them.

In several cases a more heat-resistant fibre, which retains its mechanical properties at 1000° and above, is required. These demands have stimulated work in different countries on recipes for more thermostable glass suitable for fibre production, and on practical methods for manufacturing quartz fibres. Information has been published[1] on the production of fibres containing copper oxides, which are then reduced. The presence of a film of copper or other metal on the fibre tends to increase the adhesion, especially of epoxy binders, to the fibre. The mechanical properties of glass plastics can thus be improved.

In the USSR until recently glass cloth has been mainly employed as reinforcement in constructional plastics. In countries such as the USA, England, Italy, and several others, the volume of production and demand for glass mat and rovings are growing. The use of these cheaper reinforcing materials, which do not require to be woven, allows

the technology of the production of large articles to be simplified and manufacturing processes to be mechanised. Plastics based on these fillers possess isotropic properties. A significant increase in the volume of production of glass fibre will also favour a partial transition to the use of fibre of diameter 9 μ and above, which has been achieved in the majority of countries manufacturing glass fibre. In many constructions using glass-reinforced plastics it is possible to employ fibre of diameter 9 μ and above instead of 7 μ.

For some glass-reinforced articles it is extremely important to keep the proportions of resin and glass cloth within strict limits. This task is complicated, however, by the considerable variations in the weight (±11%) and twist (7.5%) of the thread. Work has been carried out to achieve a more rigorous standardisation of the glass-fibre filling at all stages of production of the glass cloth. The results of tests on reinforced plastics made from ordinary glass cloth and from cloth based on such completely standardised materials have shown that variations in the strength and specific gravity of the plastic are thus reduced to 1.8% [1]. It is also possible in this way to minimise variations in the thickness of the cloth. Reduction of the scatter of the cloth thickness, and the production of plastics showing only small variations in density, have enabled products with optimum properties for radio purposes to be manufactured, the consumption of the starting materials (glass cloth and binder) to be reduced, and the mechanical finishing operations to be shortened. Great technological possibilities in making complicated articles have been opened up by the use of knitted glass fabrics.

Various types of binders are used in the production of glass-reinforced plastics. The most widely employed are polyester, phenol–formaldehyde, polyepoxy, and organosilicon resins. The choice of binder determines the properties of the resulting plastic and the technical methods used to manufacture goods from them. The widespread employment of reinforced plastics in different branches of industry is due in large measure to the great technological advantages of unsaturated polyesters. Plastics based on polyester resins can be moulded at low pressures and at a comparatively low temperature.

Recent work on the synthesis of new unsaturated polyesters, and binders derived from them, has been directed towards improving their physical, mechanical, and technological properties. The number of modifications of polyester–acrylates and polyester–maleates has been considerably extended, the former being prepared by esterifying dibasic acids with polyhydric alcohols and controlling the growth of the polyester chain by adding methacrylic acid. In the USSR the former type of unsaturated polyesters, developed by Berlin and his collaborators [2], has been mainly employed, together with polyester–maleates. These workers have established that it is possible to reduce the cost of polyester–acrylates. The chemical industry should be ready to widen the range of polyester–acrylates available to meet specific requirements of various branches of technology.

The main disadvantages of polyester resins in the production of glass-reinforced plastics are their flammability and in some cases inadequate thermal stability. By using halogenated polyesters and introducing special fillers it has been possible to diminish the flammability of the binders.

The thermal stability of polyester binders has been increased by using diallyl phthalate, triallyl cyanurate, and certain other compounds as the second component. Polyester binders of greater thermal stability are obtained by incorporating certain organosilicon compounds containing unsaturated groups able to copolymerise with other components of the binders.

In recent years the range of monomers which can be used to prepare polyester resins has been considerably extended. Apart from styrene, diallyl phthalate, and triallyl cyanurate, methyl methacrylate alone or mixed with styrene [3] has been used to make transparent vitreous plastics stable to light. The use of vinyltoluene improves the technological properties of the binder.

The broadening of the technological possibilities of polyester binders has contributed also to investigations on the production of various initiators, accelerators, and promoters which cause the binders to set during the moulding process at different temperatures. The peroxides of ethyl methyl ketone and cyclohexanone, lauroyl peroxide, t-butyl hydroperoxide, etc. enable polyester resins to set under indoor conditions at low temperatures.

In spite of the evident tendency for the use of polyester binders to diminish in certain stressed aircraft structures, their production is growing owing to their use in shipbuilding, carriagemaking, building, and other branches of industry.

For the production of structural parts subject to the greatest stresses, binders based on epoxy resins are being used to an increasing extent, the resulting plastics being stronger than those based on polyester resins. Epoxy resins possess good wetting power for and adhesion to glass fibres, low contraction in volume on setting, and good compatibility with various other resins, which enables their properties to be readily modified. The great advantage of epoxy binders is the possibility of carrying out moulding by both "wet" and "dry" methods. Their disadvantage is their comparatively low thermal stability. The use of epoxy binders is held back by their toxicity, which is due primarily to the toxicity of the hardeners employed. This explains the appearance of a large number of papers devoted to the search for new hardeners and methods of reducing their toxicity [4]. The thermal stability of epoxy resins can be considerably increased by modifying their properties with phenol–formaldehyde, organosilicon, furfural, and other resins [5]. Reinforced plastics based on epoxy resins hardened with adducts of hexachlorocyclopentadiene with maleic or itaconic anhydride have comparatively high thermal stability and low flammability [6]. The heat resistance of the materials is increased by the combined use of these adducts with other hardeners.

The cheapest and most readily available binders are phenol–formaldehyde resins and their modifications. The main lines of research on these binders are directed towards achieving the highest possible operating temperatures and improving their technological properties. Such research has established that constructional glass-reinforced plastics based on phenol–formaldehyde resins, which have been used for a long time at 180°–200°, can be employed for short periods at higher temperatures, up to 1000° and above.

Modification of phenol–formaldehyde resins has yielded binders with which articles can be moulded at low pressures. This has ensured that materials with good physical and mechanical characteristics have been obtained. Examples of this type of materials are the glass-fabric-reinforced plastics KAST, VFT-S, and the material AG-4 based on binders BF and VFT. The material AG-4 possesses excellent technological properties, which have ensured its

wide application. Furfural–formaldehyde binders, containing furfural as active solvent, have been successfully used to make heat-resistant large-scale components at low pressures.

Organosilicon resins, which possess high thermal stability, resistance to water, and good dielectric properties, are as yet little used in the production of constructional materials. The reason for this is the inadequate adhesion of such resins to the glass fibre, the comparatively low cohesive strength of the resin, and the resultant considerable reduction in strength on static bending at elevated temperatures. The main line of work aimed at removing the defects inherent in organosilicon polymers lies in the preparation of mixed organosilicon–organic compounds and resin compositions representing organosilicon polymers modified with organic resins. The latter method became possible as a result of the successful preparation of polysiloxane resins containing various functional groups (hydroxy, alkoxy, unsaturated, etc.). Glass-reinforced plastics which combine high thermal stability with good mechanical properties have been obtained by modifying organosilicon resins with phenol–formaldehyde, epoxy, and unsaturated polyester resins.

While one of the main tasks in the field of glass-reinforced plastics is to raise their thermal stability, a no less important problem is the necessity for stabilising their properties at increased humidities and under water. A water absorption of the order of 0.5–1.5% produces an appreciable deterioration in the mechanical properties of the material, which cannot be allowed when reinforced plastics are used in shipbuilding, aircraft construction, and other branches of technology. This explains the large amount of work devoted to eliminating this defect. Analysis of such work reveals three clear lines of approach to the improvement of the properties of glass-reinforced plastics.

The first approach is to treat the glass-fibre filler with substances which form a chemical bond with the glass, by hydrolysis of certain of its groups on the fibre surface, and a chemical bond with the binder by copolymerisation or co-condensation with constituents of the latter. Many substances suitable for this purpose have already been found, among which are Volan, a complex compound of a mixed chromium salt of methacrylic and hydrochloric acids and chromium oxychloride, vinyltrichlorosilane, vinyltriethoxysilane, and other unsaturated organosilicon compounds used for treating a glass-fibre filler when polyester binders are employed.

When phenol–formaldehyde, melamine, or epoxy resins are used in the production of glass plastics, the cloths are treated with γ-aminopropyltriethoxysilane or *m*-hydroxyphenoxy derivatives of chlorosilanes. Compounds of the latter type form the basis of general-purpose products suitable for application with various binders. They include the product of the reaction of allyltrichlorosilane or vinyltrichlorosilane with resorcinol.

The second approach to the improvement of the water-resistance of glass plastics is to introduce into the binder organosilicon monomers which react with it under certain conditions and have quite stable groups which can be hydrolysed in the presence of moisture on the surface of the glass fibre. It is possible by suitable choice of the compounds introduced into the binder not only to raise the water-resistance but also to improve the physical and mechanical properties of the plastic and increase its heat-resistance.

A third line of approach to improve water-resistance is to introduce certain substances into the fibre lubricant, emulsions of polyvinyl acetate containing silanes and Volan in particular being employed. This method, although technically the most difficult, is the most promising in our view.

The growing application of glass-reinforced plastics in various fields is due not only to the successful production of glass-fibre fillings and the synthesis of binders but also in considerable measure to the development of new methods of fabrication.

Labour requirements have been considerably reduced by the development of a continuous process for making sheet and profiles from glass cloth and mat, and various other shapes from rovings.

Reduction in labour requirements and improvement in working conditions in the manufacture of complicated articles from chopped glass fibre have been achieved by suction or blowing techniques, and centrifugal plant for the production of round articles (containers, pipes, etc.). On this equipment several processes are automatic and are accomplished without human intervention.

High-efficiency plants have been set up for the manufacture of pipes of large dimensions using both rovings and cloth. But irrational methods are often employed to make some articles, including pipes. Thus in some works making pipes the technique used for the production of bushes is adopted, consisting in winding the impregnated glass-fibre reinforcement on a mandrel, and then compressing it in a mould. The result of this technique is that the direction of the layers of reinforcement in the pipe is disturbed, and on mechanical treatment some of the layers are cut across, which in turn increases the consumption of material and diminishes the mechanical strength of the product. Reference should be made also to defects in equipment for making anisotropic glass-fibre materials, in particular at the laminated-plastics factory in Leningrad. The development of a continuous process for preparing anisotropic material of constant properties will encourage the wider application of this material in stressed structures.

In certain radio components it is important for ϵ and $\tan\delta$ to be constant over the whole article, and with some structures, it is necessary to keep the walls of the article of uniform thickness. By employing rigid dies and matrices and impregnating the glass-fibre filler in a vacuum or under pressure, it is possible to obtain an article with a close tolerance with respect to thickness and to the density of the material, which ensures that the technical radio characteristics will be constant. Impregnation in a vacuum or under pressure enables working conditions to be such that the operative can avoid contact with binders which are more or less toxic.

The introduction of new methods for processing glass-reinforced plastics and their further improvement represent an important task for workers in the plastics industry. A solution to this problem will enable the cost of such plastics to be reduced and their application in the national economy to be extended.

Table 1 gives the main physical and mechanical properties of various types of glass-fibre plastics — certain brands of glass-fabric products, the anisotropic glass-fibre material SVAM, and a plastic based on glass-fibre mat and a polyester resin.

The data in Table 2 and Figs. 1–3 give an idea of the

TABLE 1. Fundamental physical, mechanical, and dielectric properties of glass-reinforced-plastics with various binders.

Property	ST–911 polyester binder	EF32–301 epoxy–phenol binder	KAST	KST–V	VFT–S	FN phenol–formaldehyde–furfural binder	SK–9F phenol–organosilicon binder	SVAM material-multi-ply construction with epoxy resin	Plastic from glass-fibre mat and polyester resin
			modified phenol–formaldehyde binders						
Specific gravity, g/cm³	1.71	1.62—1.71	1.7—1.85	1.75—1.85	1.6—1.8	1.53—1.68	1.65—1.8	1.88—1.91	1.6—1.7
Tensile strength, kg/cm²	4345	4080	3300	3200	4000	3510	3705	4500—4700	1000—1800
Young's modulus, kg/cm²	210 000	220 000	206 000	200 000	220 000	188 500	222 500	до 350 000	80 000—100 000
Compressive strength, along the layers, kg/cm²	1537	2600	—	1000—1200	1715	1070	1610	4200	—
Static bending strength, kg/cm²	2740	4140	—	1265	3375	2135	2610	4100—4600	2000–3200
Impact strength, kg cm/cm²	525	148	80	70	105	181	145	290—310	70—80
Heat-resistance (Martens), °C	290—294	241	—	250	240	270—320	370	—	—
Water absorption after 24 h, %	0.40—0.65	0.28	1—3	0.8—1.5	1.15	1.55	0.8	—	—
Coefficient of linear expansion	$3.4—3.7 \cdot 10^{-6}$	$6.2 \cdot 10^{-6}$	—	$9 \cdot 10^{-6}$	$8 \cdot 10^{-6}$	$6.2 \cdot 10^{-6}$	$6.25 \cdot 10^{-6}$	—	—
Thermal conductivity, kcal/m h deg*	0.389—0.40	0.30	—	0.24	0.25	0.30	0.31	—	—
$\tan\delta$, at 10^{10} c/s	0.014—0.016	0.0143—0,0171	—	—	0.014—0.016	0.02	—	—	—
Dielectric constant (ϵ) at 10^{10} c/s	4.30—4.40	4.50—4.70	—	—	4.25—4.50	3.95	—	—	—
Maximum operating temp., °C	200	200	160	180—200	300	350	400	200	—
Use	structural and radio components								

* The units are not clearly stated in the original (Ed. of Translation).

position occupied by glass-reinforced plastics among other constructional materials. They possess great mechanical strength. The strength per unit weight of a glass-fabric--reinforced plastic and of anisotropic glass-fibre plastics is not inferior to, and sometimes even surpasses, those of steel, duralumin, and titanium. The disadvantage of such plastics is their comparatively low rigidity.

Glass-reinforced plastics withstand impact and dynamic loads well and are capable of damping the vibrations of structural elements. For example, the glass-fabric--reinforced plastic VFT-S will sustain without fracture more than 19 million cycles of symmetrical bending under a stress of 800 kg/cm². Similar plastics based on a polyester binder will withstand 10 million cycles of static bending under a load equivalent to 23% of their ultimate tensile strength; plastics reinforced with glass fibre mats can operate under similar conditions at a load equal to 21% of the initial strength. It must be remembered that the study of the fatigue strength and long-time strength of glass--reinforced plastics has as yet only begun. Investigation of these properties will certainly result in further improvement in the characteristics of the material by the selection of structurally the most suitable glass-fibre fillers and binders.

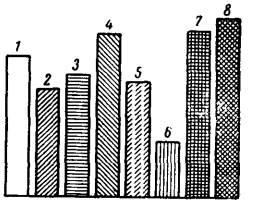


Fig. 1. Specific tensile strength of structural materials: 1) 30KhGSA steel; 2) D16 duralumin; 3) OT–4 titanium; 4) DRS pine; 5) DSP delta wood; 6) PTK fabric--reinforced plastic; 7) EF 32-301 glass-fabric-reinforced plastic; 8) SVAM.

Glass-reinforced plastics are characterised by comparatively high resistance to the action of the atmosphere, moisture, and water, which distinguishes them favourably from other plastics. The corrosion resistance of glass

TABLE 2. Mechanical properties of constructional materials.

Material	Specific gravity γ, g/cm³	Strength, kg/cm² under tension σ_b	Strength, kg/cm² under compression σ_d	Specific strength σ_b/γ	Specific strength σ_d/γ	Young's modulus E, kg/cm²	Specific rigidity E/γ
30KhGSA steel	7.85	16000	16000	2040	2040	2100 000	268 000
D–16 duralumin	2.8	4400	4400	1570	1570	720 000	257 000
OT–4 titanium	4.5	8000	8000	1775	1775	1150 000	255 000
DRS pine	0.52	1230	420	2370	810	130 000	250 000
DSP delta-wood sheet	1.25	2100	3600	1680	2920	200 000	160 000
PTK fabric-reinforced-plastic	1.35	1100	—	810	—	100 000	77 000
EF 32–301 glass-fabric-reinforced plastic	1.7	4180	3000	2400	1760	220 000	130 000
SVAM (1 : 1)	1.9	5000	4200	2600	2200	350 000	184 000

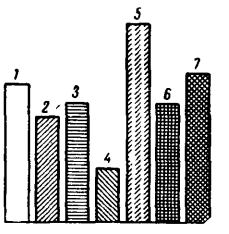


Fig. 2. Specific compressive strength of structural materials: 1) 30KhGSA steel; 2) D16 duralumin; 3) OT–4 titanium; 4) DRS pine; 5) DSP delta wood; 6) EF 32-301 glass-fabric--reinforced plastic: 7) SVAM.

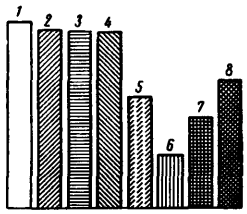


Fig. 3. Specific rigidity of structural materials: 1) 30KhGSA steel; 2) D16 duralumin; 3) OT-4 titanium; 4) DRS pine; 5) DSP delta wood; 6) PTK fabric - reinforced plastic; 7) EF 32-301 glass-fabric-reinforced plastic; 8) SVAM.

plastics is high. They possess great heat-resistance, and can operate at temperatures up to 400°, in several cases withstanding the action of a temperature of 1000° and above for short periods. The possibility of using such plastics at high temperatures is associated with their low combustibility and negligible thermal conductivity.

The combination of properties exhibited by glass-reinforced plastics has ensured their wide application in various fields of industry and technology; they can now be found even in an atomic reactor and as the roofing of industrial installations. They began to be employed in the aircraft industry earlier than in other branches of technology[7]. Up till now they have formed the main material for wireless engineering structures — radomes, surface antennae, etc. Successful work has been done on their use for important and highly stressed structural elements. Attempts are now being made to use them in jet engines, in particular for compressor blades.

The search for new materials in boatbuilding[8,9] and the employment of glass-reinforced plastics are due to the inherent defects of wood and metals. A hull made of steel or other metals corrodes under the action of seawater and requires careful protection. The repair of a metal hull or of parts of it is laborious. Boats made of glass-reinforced plastics are free from the inherent defects of those made of wood or metal: they do not rot, do not undergo corrosion, have a comparatively low water absorption, and stand up well to the action of seawater.

Glass-reinforced plastics have been used to a considerable extent in the automobile industry[10], for the production of car bodies and lorry cabs, especially for special-purpose vehicles manufactured in comparatively small numbers. The employment of these plastics in automobile construction results in a considerable reduction in the weight of the vehicle and greatly facilitates the organisation of its production. Owing to the reduction in weight it is possible to reduce the fuel consumption and to raise the carrying capacity. Cars having glass-reinforced-plastic bodies are suitable for operation in southern and northern regions. Because of the low thermal conductivity, a normal temperature is maintained inside for a longer time. Cars made of glass-reinforced plastics withstand collisions well and are less noisy than those made of metal.

Glass-reinforced plastics have also attracted attention in railway-carriage construction[11]. The use of semi-transparent plastics for the roofs and sides of carriages enables their lighting to be improved and their comfort to be increased. On account of their good heat-insulating properties, glass-reinforced plastics are employed together with foam plastics in the production of refrigerator cars; they are also successfully employed in the production of mine waggons.

The chemical industry[12] uses containers and piping made of such plastics, which have good resistance to the action of chemical reagents. In factory construction, especially for chemical works, they can be successfully used as roofing; the low weight enables that of the supporting structures to be reduced and the cost of the building to be lowered.

The above examples are far from exhausting the fields of application of glass-reinforced plastics. Here we only wish to emphasise the immense possibilities of these materials. However, their increasing use in industry demands special methods of calculation and design for articles made from them, based on a thorough consideration of their physical and mechanical properties. Only in this way is it possible to use them rationally and profitably. With new methods of calculation and design it really becomes possible to utilise glass-reinforced plastics with due regard to their lack of rigidity.

Reinforced-plastic products with a three-ply wall construction possess great rigidity, often exceeding that of metallic constructions. But the technology of the manufacture of three-layer structures is complicated and laborious. The facing materials of such structures are principally glass-reinforced plastics, while the intermediate layer can consist of plastic foams or cellular structures of impregnated paper, cotton, or glass cloth, or thin metal foil. The possibilities of cellular structures are governed to a considerable extent by the adhesives used in the production of the honeycombs and for glueing them to the facing layers.

The employment of three-ply constructions is often useful not only for increasing the rigidity of the structure but also for improving its radio-technical or thermal properties. Three-layer and multilayer structures are employed for the production of radomes and refrigerators; in boatbuilding the use of three-ply construction increases the buoyancy and the life of the boat.

The demand for new methods of calculation for structures based on glass-reinforced plastics can be satisfied only by a thorough knowledge of the properties of the material, so that study of the static, dynamic, thermal, and other characteristics acquires special importance. Such study requires in turn special methods of investigation both at normal and at elevated temperatures. Many existing methods of evaluating the properties of materials are unsuitable for glass-reinforced plastics. Creep and long-time strength, heat-resistance, fatigue limit under tension at elevated temperature and in the presence of moisture, resistance to erosion — these are far from a complete list of properties for which methods of investigation should be developed.

2. ASBESTOS-REINFORCED PLASTICS

Together with glass-reinforced plastics, asbestos-reinforced plastics have been quite widely employed during recent years as structural materials in heavy machinery, railway transport[13], and aircraft and rocket technology[7]. The growth in the application of asbestos-reinforced plastics is connected with the increased heat-resistance of fibrous asbestos fillers, which in many

cases show less loss of strength than glass fibres. New methods have been developed for processing asbestos--reinforced plastics into finished products.

The asbestos-reinforced plastic most widely used in the USSR contains asbestos cloth as reinforcing agent and phenol–formaldehyde resin as binder[14]. A wide range of components, operating under various conditions, are made from this material by mechanical processes. The disadvantage of this method is the great consumption of material and the diminution in the mechanical strength of the articles when the layers of cloth are cut. Better types of long-staple asbestos are required for the production of asbestos cloth; asbestos threads contain a certain amount of cotton fibre, which reduces the heat-resistance of plastics that incorporate them.

Asbestos fibres are used in moulding compositions K6, KFZ, K41–5, etc., from which components for various purposes and Faolite for the chemical industry[15] are produced. Asbestos paper and board are more economical fillers and are now successfully employed for the preparation of laminated plastics, the mechanical and dielectric properties of which differ little from those of fabric--reinforced plastics and depend also on the type of resin (Table 3). The plastics based on paper have a greater fatigue strength than the fabric-reinforced materials[16].

Since impregnated asbestos paper and board cannot be stretched, they can be used only for making flat articles. Several methods exist for making products of complex shape[17], including a process similar to paper making; asbestos fibre is suspended in a large volume of water, and the binder is introduced into the suspension. The lower part of the apparatus contains a gauze form. On evacuation the fibre and the binder are distributed over the surface of the form. After a layer of the required thickness has been formed, the product is drained, dried, and pressed. The binder should form an emulsion or a suspension in water. Phenol–formaldehyde, polyester, and epoxy resins are used as binders.

Similar products can be made also from intermediates obtained by preliminary moulding. The equipment employed for this purpose is similar to that for suction of glass fibres: the asbestos fibres in a closed chamber are sucked on to the surface of a perforated form shaped like the required article. Before removal from the form, the half-finished product is sprayed with binder to give it the minimum strength required for subsequent impregnation and moulding.

Asbestos mats, made on asbestos-carding machines, are very widely used as filler. These mats consist of laminated material with a mainly parallel arrangement of the fibres, and sometimes contain a certain amount of glass fibre. The mats are impregnated with a phenolic, melamine, polyester, or epoxy resin. They are moulded at a comparatively low pressure. In the USA such mats appear on the market under the name Pyrotex, and in England as Durestos[17].

As already noted, various binders are now used in the production of asbestos-reinforced plastics. Structural materials with the greatest heat resistance are obtained with phenol–formaldehyde resins. Workers who have studied the properties of such plastics hold different opinions as to their thermal stability. This is probably due both to different methods of determining the thermal stability of the material and to the different demands made on the articles. In any case, it may be expected that asbestos--reinforced plastics with phenol–formaldehyde binders can operate for long periods at 200°–250°, for short periods at 400°–500°, and for a few seconds during unilateral heating to 2500°–2750°[17–19]. At 540° and above the properties of the material deteriorate appreciably because the asbestos loses water of crystallisation.

TABLE 3. Properties of laminated asbestos-reinforced plastics made with different resins[16] (Czechoslovakia, Eastern Germary, Great Britain, USA).

Property	Phenolic resin		Melamine resin		Organosilicon resin	
	cloth	board	cloth	board	cloth	board
Specific gravity, g/cm³	1.5—1.8	1.5—1.83	1.75—1.85	1.75—1.85	1.75	1.65
Water absorption at equal thickness, %	0.4—3.0	0.3—5.0	0.4—5.0	0.4—5.0	—	1.0
Tensile strength, kg/cm² across the warp	400—840	350—1050	455—840	455—910	410	800
along the warp	400—700	560—900	—	1050	—	--
Compressive strength, kg/cm² perpendicular to layers	1260—3150	800—2800	1890—3500	2450—2660	2310	1000
parallel to layers	1400—1470	1190	—	—	—	—
Bending strength, kg/cm² along the warp	700—2450	700—2450	1190—1680	1190—2100	840	1400
across the warp	800—980	770—1400	—	2450	—	—
Shearing strength, kg/cm²	770	—	—	—	1260	—
Young's modulus, kg/cm²	24000—119000	25000—175000	—	—	—	—
Cleavage strength, kg	280	120	—	—	—	—
Heat-resistance (Martens), °C	160—250	160—200	100—205	100—205	—	250
Long-time (200 h), heat-resistance, °C	135—150	135	108—250	108—250	—	—
Coefficient of linear thermal expansion × 10⁶	1.5—1.7	1.5	—	—	—	—
Breakdown voltage, kV/mm	2.5	4.0	2.5—5.0	2.5—5.0	—	6—7
Tangent of dielectric loss angle at 10^6 c/s	0.115	0.115	0.12—0.22	0.12—0.22	—	0.15 (at 800 c/s)

3. PLASTICS BASED ON ORGANIC FIBRES

The widespread use of glass and asbestos-reinforced plastics as structural materials does not mean that all the possibilities of improving the properties and increasing the use of plastics based on organic-fibre reinforcement have now been exhausted. Continual improvements in fillers, binders, and processing techniques have enabled new applications to be found for such materials.

Let us cite a few examples: plastics based on polyester resins and glass fibres have been successfully used in Eastern Germany[20] for experimental car models. Economic analysis showed, however, that it was more economical in the mass production of the bodies to use as reinforcement a cotton by-product in the form of a special mat, and as binder powdered phenolic–cresolic resins, which were introduced into the mat during its preparation. Components of the body are formed under a pressure of 50 kg/cm² at 150°–160°. Among the characteristics of such material are a static bending strength of 1200–1500 kg/cm², a specific impact strength of 25–30 kg cm/cm², a modulus of elasticity of 83 000 kg/cm², and a specific gravity of 1.36 g/cm³.

Recently a report has appeared in the literature[21] on the material Resnit, which is a knitted fabric impregnated

with a phenol–formaldehyde resin. Articles are made from this material by cutting out lengths from the impregnated fabric, assembling a pile of the required thickness, and compressing it under 7–35 kg/cm² at 160°. The process of pressing out articles from such material resembles the deep drawing of metals, and is carried out on similar plant. It has been reported that the material can be used successfully in the large-scale manufacture of cars.

Great possibilities in the production of constructional plastics are opened up by reinforcement with cloth made of synthetic fibres (polyamide and polyester). A thorough study of the properties of such plastics, especially at high temperatures, will enable the field of application of plastics in general to be extended, and especially their use as heat-insulating materials. The first tests on such materials at 2500°–3000° and above have shown that their loss in weight in the intense heat is less than that of materials reinforced with glass or asbestos fabrics.

With the widespread manufacture of synthetic fibres, plastics based on them may also find application in the production of large bearings, various shock-absorbing components, and other articles. Polyamides can also be employed independently as structural materials, e.g. for the propellers of boats. Articles can be made from them both mechanically and by pressure moulding.

4. WOOD-FILLED PLASTICS

Wood-filled plastics have been used for a long time in the national economy of the Soviet Union[15] and it is impossible to ignore these materials in a review of constructional plastics. Their manufacture is supported by a practically inexhaustible source of raw material. Wood-filled plastics are sold in the form of sheets and slabs, from which a variety of components can be made by machining, e.g. rotors for helicopters and airscrews for light aeroplanes; in the form of impregnated veneers, from which bushes for bearings, couplings, and other components are pressed; in the form of thermoplastic materials, such as Berolite, which can be reprocessed to finished products by hot pressing. Wood-filled plastics based on furfural–acetone resins may find wide application; they are less inflammable.

Wood-filled plastics will no doubt find increasing employment in carriage construction, heavy machinery, and the production of technological equipment.

The questions considered in this review by no means exhaust all the problems of the production and application of structural plastics; no attempt has been made to consider more than a few of them.

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ACYLOXYSILANES

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INTRODUCTION

The term acyloxysilanes in this review denotes monomeric organosilicon compounds in which the silicon atom is joined to at least one acyloxy group. Known types of acyloxysilanes are the tetraacyloxysilanes of general formula $Si(OCOR)_4$, alkylacyloxysilanes $R_xSi(OCOR')_{4-x}$, alkoxyacyloxysilanes $(RO)_xSi(OCOR')_{4-x}$, alkylalkoxyacyloxysilanes $R_x(R'O)_ySi(OCOR'')_{4-x-y}$, and acyloxytrichlorosilanes $Cl_3SiOCOR$. Compounds such as aminoacyloxysilanes, $(NH_2)_xSi(OCOR)_{4-x}$, and (alkylthio)acyloxysilanes, $(RS)_xSi(OCOR')_{4-x}$ are not known.

The first acyloxysilane known was tetraacetoxysilane, prepared by Friedel and Ladenburg[1] in 1868, but up to 1947, i.e. in the 80 years since this class of compound was discovered, no more than 15 papers appeared on the subject, these relating mainly to methods for the preparation of certain acyloxysilanes. Interest in acyloxysilanes in subsequent years has grown considerably, since many have found wide practical application. Thus tetraacyloxysilanes are used in the pharmaceutical industry[2], and their polymeric acylated partial-hydrolysis products are used for the preparation of materials impregnated with silicon dioxide[3].

Alkylacyloxy- and alkylalkoxyacyloxysilanes are widely used to give water-repellent properties to various materials[4-14]. The hydrophobic properties obtained with these reagents are retained for longer periods than those obtained with other organosilicon compounds[15]. Another advantage of acyloxysilanes over, for instance, chlorosilanes arises in their hydrolysis: they do not form corrosive substances such as hydrochloric acid, so that they can be used to impart hydrophobic properties to wool, silk, cotton, leather, wood, paper, iron, magnesium, and other metals[9-12,16-19]. Fabrics impregnated with alkylacyloxysilanes are stable to laundering[9]. Acyloxysilanes, in the wider sense of the term, are also used as plasticisers for lacquers, anti-corrosive and insulating coatings, for the preparation of adhesives, for lubricants and paints withstanding high temperatures, and for the preparation of plastic foams[20-24]. For the analysis of certain volatile organosilicon compounds, the corresponding acetoxy derivatives are prepared[25].

In the last 10–12 years more than 100 papers, theoretical and applied, have been published relating to the synthesis, properties, and uses of acyloxysilanes.

I. METHODS OF PREPARATION OF ACYLOXYSILANES

1. Tetraacyloxysilanes and Acyloxytrichlorosilanes

The simplest, most convenient, and therefore the most used method for the preparation of tetraacyloxysilanes — mixed anhydrides of orthosilicic and organic acids — is the replacement by acyloxy groups of the chlorine of silicon tetrachloride, which is a cheap and readily available industrial material.

In 1868 Friedel and Ladenburg[1] heated a mixture of silicon tetrachloride and a slight excess of acetic acid until no more hydrogen chloride was evolved, and obtained tetraacetoxysilane:

$$SiCl_4 + 4CH_3COOH \longrightarrow Si(OCOCH_3)_4 + 4HCl.$$

Tetrabutyryloxysilane was obtained analogously in 76.6% yield[26]. Later, the method was slightly modified, the reaction being carried out in an inert solvent: in n-heptane, tetraacetoxysilane was obtained in 82% yield and tetrapropionyloxysilane in 80% yield[3], in ether, tetraacetoxysilane in 30% yield[27], and in benzene, tetraformyloxysilane[28] and tetrabenzoyloxysilane in quantitative yield[29]. The tetraacyloxysilanes derived from mono-, di-, and trichloroacetic acids were obtained in benzene in 90–99% yield[30].

The addition of pyridine to the reaction mixture accelerates the reaction and increases the yields of tetraacyloxysilanes[31]. Thus in benzene the tetraacyloxysilanes derived from the following acids were obtained: acetic (96.9% yield), phenylacetic (95.7%), benzoic (97.8%); in n-heptane, n-heptanoic (99.7%), isobutyric (78.2%), isovaleric (88%), and trimethylacetic (86.2%).

Saturated dibasic acids react with silicon tetrachloride in benzene to form acid monoanhydrides of the organic acid with silicic acid, each of the four acid residues attached to the silicon retaining a free carboxyl group[32]:

$$4HOOC[CH_2]_nCOOH + SiCl_4 \longrightarrow Si(OCO[CH_2]_nCOOH]_4 + 4HCl.$$

The hydroxy group of organic hydroxyacids reacts with silicon tetrachloride more easily than the carboxy group, the products being alkoxy- and not acyloxysilanes[33,34]::

$$SiCl_4 + 4HO\,RCOOH \longrightarrow Si(ORCOOH)_4 + 4HCl.$$

However, salicylic acid gives a polymeric reaction product of general formula $[(OC_6H_4COO)_2Si]_n$, indicating that in this case both the hydroxy and carboxy groups react. The reaction of 1 mole of silicon tetrachloride with 4 moles of salicylic acid gave the same reaction product, but in 50% yield[35].

Silicon tetrabromide may be used instead of silicon tetrachloride; tetrabenzoyloxy- and tetrastearoyloxysilanes were prepared in this way[36-38].

The sodium salts of organic acids (with the exception of the formate) react with silicon tetrachloride analogously to the acids themselves, giving the tetraacyloxysilanes[39-41]:

$$4RCOONa + SiCl_4 \longrightarrow Si(OCOR)_4 + 4NaCl.$$

Boiling the mixture of reagents in ether gave, in yields of 58.8–83.8%, the tetraacyloxysilanes derived from propionic, butyric, trichloroacetic, crotonic, stearic, cinnamic, hydrocinnamic, benzoic, *o*-chlorobenzoic, *p*-hydroxybenzoic, and α-naphthoic acids. Tetraacetoxysilane has also been prepared by the reaction of silicon tetrachloride with silver acetate (23%) and lead acetate[27].

A convenient method for the synthesis of tetraacyloxysilanes, particularly crystalline ones, is by the reaction of silicon tetrachloride with an excess of the acid anhydride. The reaction is exothermic; on cooling, the tetraacyloxysilane crystallises, and can be separated by filtration and purified by recrystallisation from the acid anhydride; yields of up to 84.5% are obtained[1,42,43]:

$$4(RCO)_2O + SiCl_4 \longrightarrow Si(OCOR)_4 + 4RCOCl,$$

where R = CH_3 or C_6H_5.

To accelerate the formation of the tetraacetoxysilane, it has been recommended to add thallium acetate, which reacts with the acetyl chloride formed and removes it from the reaction mixture[44]:

$$CH_3COCl + TlOCOCH_3 \longrightarrow TlCl + (CH_3CO)_2O.$$

Tetraacetoxysilane and an alkyl halide are obtained by the reaction of silicon tetrachloride with lower alkyl (up to pentyl) acetates[45]:

$$4CH_3COOR + SiCl_4 \longrightarrow Si(OCOCH_3)_4 + 4RCl.$$

The reaction is different with the acetates of other alcohols and of phenols:

$$4CH_3COOR + SiCl_4 \longrightarrow Si(OR)_4 + 4CH_3COCl$$

where R = iso-C_5H_{11}, C_6H_5, or *p*-$CH_3C_6H_4$;

$$2CH_3COOR + SiCl_4 \longrightarrow 2CH_3COCl + 2RCl + SiO_2,$$

where R = $C_6H_5CH_2$ or $C_6H_5CH_2CH_2$.

However, the literature has indications that completely pure esters not containing traces of moisture do not react with silicon tetrachloride. This has been reported by Ladenburg[46], Rauter[47], and by Yur'ev et al.[48-50], who showed, for example, that silicon tetrachloride reacts with the acid ethyl esters of dibasic acids to form the tetraacyloxysilanes of general formula $Si(OCO[CH_2]_nCOOC_2H_5)_4$.

The synthesis of tetraacyloxysilanes from trichlorosilane and organic acids in an inert organic solvent, e.g n-heptane[3], is of theoretical interest and great practical significance:

$$HSiCl_3 + 4RCOOH \longrightarrow Si(OCOR)_4 + 3HCl + H_2;$$

the acyloxy groups replace the hydrogen atom of the trichlorosilane as well as the chlorine atoms.

The sulphides may also be used for the synthesis of tetraacyloxysilanes[51,52] as well as silicon halides: the tetraacyloxysilanes derived from acetic (25% yield), monochloroacetic (11.5% yield), stearic, and benzoic acids have been prepared by reacting the acids with silicon sulphide:

$$SiS_2 + 4RCOOH \longrightarrow Si(OCOR)_4 + 2H_2S.$$

The tetraacyloxysilanes derived from saturated mono basic acids containing at least six carbon atoms and from aromatic acids such as benzoic and naphthoic can be prepared by a trans-acylation reaction between the acids and tetraacetoxysilane[2,36-38]:

$$Si(OCOCH_3)_4 + 4RCOOH \longrightarrow Si(OCOR)_4 + 4CH_3COOH,$$

$$Si(OCOCH_3)_4 + 2(RCO)_2O \longrightarrow Si(OCOR)_4 + 2(CH_3CO)_2O.$$

The above are the main methods for the synthesis of tetraacyloxysilanes.

The first acyloxytrichlorosilane to be discovered was acetoxytrichlorosilane, first prepared by Goubeau and Mundiel[27] in 20% yield by the action of excess silicon tetrachloride on sodium acetate:

$$SiCl_4 + CH_3COONa \longrightarrow Cl_3SiOCOCH_3 + NaCl.$$

Yur'ev et al.[53-56] showed that acyloxytrichlorosilanes are formed in quantitative yields by the action of excess silicon tetrachloride on monobasic organic acids of the aliphatic, aromatic, and heterocyclic series:

$$RCOOH + SiCl_4 \longrightarrow RCOOSiCl_3 + HCl,$$

where (1) R = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, iso-C_4H_9, t-C_4H_9, n-C_5H_{11}, or n-C_7H_{15};

(2) R = C_6H_5, *o*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$, *o*-ClC_6H_4, *p*-ClC_6H_4, *o*-$NO_2C_6H_4$, *m*-$NO_2C_6H_4$, *p*-$NO_2C_6H_4$, α-$C_{10}H_7$;

(3) R = α-C_4H_3O, α-C_4H_3S.

A necessary condition for the preparation of acyloxytrichlorosilanes is that the reaction be conducted in the liquid phase; the acid must be soluble in silicon tetrachloride or its mixtures with inert solvents such as acetone and ether. Acids which are not soluble in silicon tetrachloride form only tetraacyloxysilanes when heated with it:

$$4\,RCOOH + SiCl_4 \longrightarrow Si(OCOR)_4 + 4\,HCl,$$

where R = p-ClC_6H_4, o-$NO_2C_6H_4$, p-$NO_2C_6H_4$.

Acyloxytrichlorosilanes may also be prepared from excess silicon tetrachloride and the tetraacyloxysilanes, for example, benzoyloxytrichlorosilane in 53.5% yield from tetrabenzoyloxysilane[53]:

$$(C_6H_5COO)_4Si + 3\,SiCl_4 \longrightarrow 4\,C_6H_5COOSiCl_3.$$

Goubeau and Mundiel[27] were unable to obtain acetoxytrichlorosilane from excess silicon tetrachloride and acetic acid or tetraacetoxysilane; in the first case they obtained only tetraacetoxysilane, and made the correct deduction that the acetoxytrichlorosilane formed (I) is unstable and disproportionates to tetraacetoxysilane and silicon tetrachloride (II), hydrogen chloride favouring this reaction:

$$CH_3COOH + SiCl_4 \longrightarrow CH_3COOSiCl_3 + HCl, \quad (I)$$

$$4\,CH_3COOSiCl_3 \rightleftharpoons 3\,SiCl_4 + Si(OCOCH_3)_4. \quad (II)$$

In the second case, in addition to the starting materials, the authors separated acetyl chloride and an organosilicon compound in which the Si : Cl ratio varied in different experiments but was approximately 2 : 3. This compound could not be studied in more detail, because attempts to purify it by distillation caused decomposition to acetyl chloride and acetic anhydride. The following possible conversion reactions were suggested:

$$2\,Cl_3SiCl + 2\,CH_3COOSi(OCOCH_3)_3 \xrightarrow{-CH_3COCl} 2\,Cl_3SiOSi(OCOCH_3)_3 \rightarrow$$

$$\xrightarrow{-(CH_3CO)_2O} Cl_3Si{-}O{-}\underset{\displaystyle COCH_3O}{\overset{\displaystyle OCOCH_3}{\underset{|}{\overset{|}{Si}}}}{-}O{-}\underset{\displaystyle COCH_3O}{\overset{\displaystyle OCOCH_3}{\underset{|}{\overset{|}{Si}}}}{-}O{-}SiCl_3 \longrightarrow \text{etc.}$$

Two main reactions take place:

$$\equiv Si{-}Cl + CH_3COO{-}Si\equiv \longrightarrow \equiv Si{-}O{-}Si\equiv + CH_3COCl,$$

$$2\equiv Si{-}OCOCH_3 \longrightarrow \equiv Si{-}O{-}Si\equiv + (CH_3CO)_2O.$$

Depending on the excess of silicon tetrachloride, different reaction products are obtained.

The possibility of this type of reaction was also shown by Kapoor et al.[57], who suggested that the formation of acetyl chloride in the reaction of silicon tetrachloride with acetic acid takes place as follows:

$$ClSiCl_3 + 3\,CH_3COOH \longrightarrow ClSi(OCOCH_3)_3 + 3\,HCl,$$

$$SiCl_4 + 4\,CH_3COOH \longrightarrow Si(OCOCH_3)_4 + 4\,HCl,$$

$$ClSi(OCOCH_3)_3 + Si(OCOCH_3)_4 \longrightarrow O\begin{<}\begin{matrix}Si(OCOCH_3)_3\\ \\ Si(OCOCH_3)_3\end{matrix} + CH_3COCl.$$

Hexaacetoxydisiloxane has not been obtained pure, but from analytical data on the silicon and chlorine contents of the product, the authors suggested that they were working with mixtures of hexaacetoxydisiloxane with triacetoxychlorosilane and tetraacetoxysilane.

2. Alkyl- and Arylacyloxysilanes

In this group alkylacyloxysilanes have been described in most detail in the literature, the majority of papers being concerned with alkylacetoxysilanes.

Alkylacyloxysilanes, like the tetraacyloxysilanes, are most often prepared by substituting the acyloxy group for the chlorine in the corresponding alkylhalogenosilanes by reaction with acids or their salts or anhydrides. Thus boiling monobasic organic acids for 40–85 h with excess triethylchlorosilane has given the triethylacyloxysilanes in 26–52% yield[58]:

$$(C_2H_5)_3SiCl + RCOOH \longrightarrow (C_2H_5)_3SiOCOR + HCl,$$

where R = C_3H_7, iso-C_4H_9, or C_6H_{13}.

Dibasic organic acids react with trialkylchlorosilanes under the same conditions as follows[58]:

$$2\,R_3SiCl + HOOC(CH_2)_n COOH \longrightarrow R_3SiOCO(CH_2)_n COOSiR_3 + 2\,HCl,$$

where R = C_2H_5, n = 2, 4, or 7; R = CH_3, n = 4 or 7.

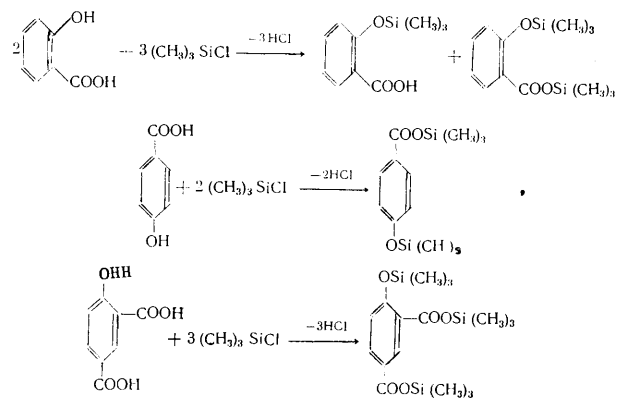
Monobasic amino-acids do not react with trimethylchlorosilane, but dibasic amino-acids and benzoylated monobasic amino-acids react to give the corresponding acyloxysilanes[59]:

$$\begin{matrix}HOOC\\ NH_2\end{>}R{-}COOH + (CH_3)_3SiCl \xrightarrow{-HCl} \begin{matrix}HOOC\\ NH_2\end{>}R{-}COOSi(CH_3)_3,$$

$$C_6H_5CONHCH_2COOH + (CH_3)_3SiCl \xrightarrow{-HCl} C_6H_5CONHCH_2COOSi(CH_3)_3.$$

To accelerate the reaction between alkylhalogenosilanes and organic acids and to increase the yields of alkylacyloxysilanes, it has been recommended to carry out the reaction in benzene in the presence of pyridine[60] or in pyridine (yield 65–76%)[61]; according to the patent literature, the same results are achieved in the presence of salts and anhydrides of the organic acids[4,62,63].

With aromatic hydroxy-acids (salicylic, p-hydroxybenzoic, and 1-hydroxyisophthalic[64]) both the hydroxy and carboxy groups react with trimethylchlorosilane; in pyridine the reaction takes place at room temperature:



The replacement of the halogen by the acyloxy group in alkylhalogenosilanes is much more conveniently carried out by the action of salts of the organic acids (usually the sodium[5,6,65–69], potassium[58,70–72], or silver[73–77] salts),

$$R_xSiHal_{4-x} + (4-x)\,R'COOM \longrightarrow R_xSi(OCOR')_{4-x} + (4-x)\,MHal,$$

by boiling the alkylhalogenosilane with an excess of the salt (sometimes an excess of the silane is used[69]) in the absence

of a solvent or in the presence of inert solvents (benzene[75], toluene[58], ligroin[71], petroleum ether[67,68]). Yields are 40–93%. The reaction is very vigorous with the lower alkylhalogenosilanes. Alkylhalogenosilanes with a long carbon chain (more than eight) react in 10–20 h at 60°–120° in a solvent (ether, toluene)[15]. It is sometimes better to alter the procedure slightly; for example, the yield of dimethyldiacetoxysilane was increased from 50%[65] to 76% when the reaction was effected by circulating dimethyldichlorosilane vapour over sodium acetate[69].

Another interesting reaction is the preparation of diphenyldiacyloxysilanes from diphenyldichlorosilane and alkylacyloxy derivatives of germanium[75]:

$$2C_2H_5Ge(OCOR)_3+3(C_6H_5)_2SiCl_2 \longrightarrow 2C_2H_5GeCl_3\downarrow+3(C_6H_5)_2Si(OCOR)_2.$$

Alkylacyloxysilanes, including those with unsaturated hydrocarbon radicals, may also be prepared by the action of acid anhydrides on alkylhalogenosilanes:

$$R_xSiHal_{4-x}+(4-x)(R'CO)_2O \longrightarrow R_xSi(OCOR')_{4-x}+(4-x)R'COHal.$$

This method has been used almost exclusively for the preparation of alkylacetoxysilanes. The reaction has most often been accomplished by long standing (12–96 h) of the reaction mixture at room temperature[69,72,78–83]; sometimes boiling[7,84,85] or the addition of triethanolamine as catalyst[86–88] is required. Yields are 70–98%. Heating is resorted to only in cases of extreme necessity, since it apparently favours side reactions in which siloxanes are formed. For example, the reaction of dichlorophenyltrichlorosilane with acetic anhydride at room temperature produces dichlorophenyltriacetoxysilane, but at 55° bis(dichlorophenyl)tetraacetoxydisiloxane is obtained[83]:

$$Cl_2C_6H_3SiCl_3+3(CH_3CO)_2O \xrightarrow{20^\circ} Cl_2C_6H_3Si(OCOCH_3)_3+3CH_3COCl,$$

$$2Cl_2C_6H_3SiCl_3+5(CH_3CO)_2O \xrightarrow{55^\circ} [Cl_2C_6H_3Si(OCOCH_3)_2]_2O+6CH_3COCl.$$

Trialkylacetoxysilanes may also be prepared by acetylating the corresponding trialkylsilanols with acetic acid (up to 80% yield)[89], acetic anhydride[90,91], or acetyl chloride[78,92]:

$$R_3SiOH+CH_3COOH \longrightarrow R_3SiOCOCH_3+H_2O,$$

where R = C_6H_5

$$R_3SiOH+(CH_3CO)_2O \longrightarrow R_3SiOCOCH_3+CH_3COOH,$$

where R = C_2H_5 or C_6H_5

$$R_3SiOH+CH_3COCl \longrightarrow R_3SiOCOCH_3+HCl,$$

where R = C_6H_5.

If in the reaction with triphenylsilanol the acetyl chloride is used in greater than stoichiometric amounts, triphenylchlorosilane is formed as a result of a side reaction between the triphenylacetoxysilane and acetyl chloride[78]:

$$(C_6H_5)_3SiOCOCH_3+CH_3COCl \longrightarrow (C_6H_5)_3SiCl+(CH_3CO)_2O.$$

This was confirmed by the preparation of triphenylchlorosilane from triphenylacetoxysilane and acetyl chloride. The reason why attempts to prepare trialkylacyloxysilanes by reaction between the corresponding silanols and acid chlorides were unsuccessful[93] is apparently that excess acid chloride was used. The opinion of Kipping and Lloyd[92] that acetic anhydride does not react with triphenylsilanol, even in the presence of zinc chloride, is thus clearly erroneous.

Sodium derivatives of the silanols also react with acetyl chloride[78]:

$$(C_6H_5)_3SiONa+CH_3COCl \longrightarrow (C_6H_5)_3SiOCOCH_3+NaCl.$$

Hexaalkyldisiloxanes (but not hexaphenyldisiloxanes) are decomposed by the action of the anhydrides of monobasic organic acids on boiling in the presence of zinc chloride, forming trialkylacyloxysilanes in 90% yield:

$$R_3SiOSiR_3+(R'CO)_2O \longrightarrow 2R_3SiOCOR'.$$

Under these conditions, the anhydrides of dibasic acids (succinic, maleic) do not react[94]. Trialkylalkoxysilanes react with acetic anhydride in the presence of a catalyst (sulphuric acid[78]) or in its absence[95,96], to produce trialkylacetoxysilanes:

$$R_3SiOR'+(CH_3CO)_2O \longrightarrow R_3SiOCOCH_3+CH_3COOR'.$$

The reaction of trialkylalkoxysilanes with benzoyl chloride produces trialkylchlorosilanes[96]:

$$R_3SiOR'+C_6H_5COCl \longrightarrow R_3SiCl+C_6H_5COOR'.$$

The replacement of ethoxy groups by acetoxy groups also takes place by the reaction of dimethyldiethoxysilane with diacetoxymethane in the presence of sulphuric acid, the products being dimethyldiacetoxysilane and ethylal[97]:

$$(CH_3)_2Si(OC_2H_5)_2+(CH_3COO)_2CH_2 \longrightarrow (CH_3)_2Si(OCOCH_3)_2+(C_2H_5O)_2CH_2.$$

The reaction of trialkylsilanes with organic acids to produce trialkylacyloxysilanes was first proposed and studied in detail by Dolgov et al.[98]:

$$R_3SiH+R'COOH \longrightarrow R_3SiOCOR'+H_2.$$

This reaction is catalysed by sulphuric acid, hydrogen iodide, and iodine, but best of all by a mixture of aluminium and iodine; the rate of reaction increases with increase of the dissociation constant of the acid. Formic acid reacts anomalously with triethylsilane, forming hexaethyldisiloxane, although the reaction is accompanied by the evolution of hydrogen. The following mechanism for the reaction between trialkylsilanes and organic acids was suggested:

$$R_3SiH+I_2 \longrightarrow R_3SiI+HI,$$

$$R_3SiH+HI \xrightarrow{AlI_3} R_3SiI+H_2,$$

$$R_3SiI+HOCOR' \longrightarrow R_3SiOCOR'+HI.$$

The yields of trialkylacyloxysilanes are 81–87%.

Alkylsilanes also form alkylacetoxysilanes by reaction with mercury acetate[98,99] or silver acetate[77]. Triethylsilane and mercury acetate gave triethylacetoxysilane in yields of 72.5–91%:

$$(C_2H_5)_3SiH+Hg(OCOCH_3)_2 \longrightarrow (C_2H_5)_3SiOCOCH_3+Hg+CH_3COOH.$$

Alkylacetoxysilanes are also obtained by the reaction of acetic anhydride with alkylaminosilanes[71]:

$$R_xSi(NHR')_{4-x}+(4-x)(CH_3CO)_2O \longrightarrow R_xSi(OCOCH_3)_{4-x}+(4-x)CH_3CONHR',$$

where R' = hydrogen or alkyl.

Anderson and Fischer[77] found that alkylsilane derivatives such as the sulphides, cyanides, isocyanates, and isothiocyanates react metathetically with silver salts of organic acids, giving the alkylacyloxysilanes:

$$[(C_2H_5)_3Si]_2S+2AgOCOCH_3 \longrightarrow 2(C_2H_5)_3SiOCOCH_3+Ag_2S,$$

$$(C_2H_5)_3SiCN+AgOCOCF_3 \longrightarrow (C_2H_5)_3SiOCOCF_3+AgCN,$$

$$(CH_3)_2Si(CNO)_2+2AgOCOCF_3 \longrightarrow (CH_3)_2Si(OCOCF_3)_2+2AgCNO,$$

$$(C_2H_5)_2Si(CNS)_2+2AgOCOR \longrightarrow (C_2H_5)_2Si(OCOR)_2+2AgCNS,$$

where R = CH_3 or CF_3.

For the preparation of alkylacyloxysilanes wherein the acyloxy group is derived from an acid of low volatility, it is sometimes convenient to trans-acylate the alkylacyloxysilanes formed by more volatile acids, by heating with the organic acid while slowly distilling off the more volatile acid[76,77,100]:

$$R_xSi(OCOR')_{4-x} + (4-x)\,R''COOH \longrightarrow R_xSi(OCOR'')_{4-x} + (4-x)\,R'COOH\uparrow.$$

Finally, an interesting reaction from the theoretical point of view is the preparation of triphenylformyloxysilane in 40–55% yields by the thermal rearrangement at 190° of triphenylsilane carboxylic acid[60]:

$$(C_6H_5)_3Si-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{190^\circ} (C_6H_5)_3Si-O-\underset{\underset{O}{\|}}{C}-H.$$

By-products of this reaction are hexaphenyldisiloxane (57% yield), formic acid, and carbon monoxide.

3. Alkylalkoxyacyloxy- and Alkoxyacyloxysilanes

Alkylalkoxyacyloxy- and alkoxyacyloxysilanes are obtained in 14–34% yield by heating alkylalkoxy- and alkoxysilanes respectively with acid anhydrides[101,102]:

$$R_xSi(OR')_{4-x} + y\,(R''CO)_2O \longrightarrow R_xSi(OR')_{4-x-y}(OCOR'')_y + y\,R''COOR',$$

where x = 0, 1, or 2, and y = 1, 2, or 3.

The low yields are due to the dissociation of the reaction products in the anhydride medium, so that a side reaction leading to the formation of polyorganosiloxanes takes place[101], e.g.:

$$C_2H_5Si(OR)_2(OCOCH_3) \xrightarrow{(CH_3CO)_2O} C_2H_5Si(OR)_2O^- + CH_3CO^+,$$

$$C_2H_5Si(OR)_2(OCOCH_3) \xrightarrow{(CH_3CO)_2O} C_2H_5Si(OR)(OCOCH_3)^+ + (OR)^-,$$

$$C_2H_5Si(OR)(OCOCH_3)^+ + C_2H_5Si(OR)_2O^- \longrightarrow (C_2H_5)(RO)(CH_3COO)Si-O-Si(OR)_2C_2H_5.$$

The formation of polysiloxanes may become the main reaction in the reaction of alkylalkoxysilanes or alkoxysilanes with phthalic anhydride[103].

When a trialkoxysilane reacts with acetic anhydride[104], one alkoxy group is first replaced by the acyloxy group to form a dialkoxyacyloxysilane; with further heating and with excess acetic anhydride, the reaction proceeds further, with substitution of the hydrogen atom to produce a dialkoxydiacyloxysilane:

$$(RO)_3SiH + (CH_3CO)_2O \rightarrow (RO)_2SiH(OCOCH_3) + CH_3COOR,$$

$$(RO)_2SiH(OCOCH_3) + (CH_3CO)_2O \rightarrow (RO)_2Si(OCOCH_3)_2 + CH_3CHO.$$

The literature contains contradictory reports on the action of organic acids on alkoxysilanes. According to some[105,106], alkoxyacyloxysilanes and the corresponding alcohols are formed:

$$Si(OR)_4 + R'COOH \rightarrow (RO)_3SiOCOR' + ROH,$$

while others[20,107] assert that the reaction produces esters and silicic acid:

$$Si(OR)_4 + 4R'COOH \rightarrow 4R'COOR + Si(OH)_4.$$

These differences are apparently due to the different reaction conditions.

Alkoxyacyloxysilanes can also be obtained by the action of organic acids on alkoxyaminosilanes[108]:

$$(RO)_2Si(NH_2)_2 + 4R'COOH \rightarrow (RO)_2Si(OCOR')_2 + 2R'COONH_4.$$

The specific method of substituting the alkoxy group for the acyloxy group in acyloxysilanes containing at least two acyloxy groups can also be used for the synthesis of alkoxyacyloxy- and alkylalkoxyacyloxysilanes. The reaction of acyloxysilanes with primary and secondary alcohols is exothermic; the acid liberated in the reaction should be distilled off at as low a temperature as possible[69,70,81,109,110]. Tertiary alcohols react only by heating to 100°–140°[69,110]:

$$R_xSi(OCOR')_{4-x} + yR''OH \rightarrow R_xSi(OCOR')_{4-x-y}(OR'')_y + yR'COOH.$$

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All these methods for the synthesis of acyloxysilanes (with the exception of the last) involve the replacement by an acyloxy group of various atoms or radicals joined to the silicon atom. They may be represented schematically as follows:

(1) $\equiv Si-Hal \xrightarrow{+RCOOH,\ RCOOM,\ (RCO)_2O} \equiv Si-OCOR$,

(2) $\equiv Si-H \xrightarrow{+RCOOH,\ RCOOM,\ (RCO)_2O} \equiv Si-OCOR$,

(3) $\equiv Si-OH \xrightarrow{+RCOOH,\ (RCO)_2O,\ RCOCl} \equiv Si-OCOR$,

(4) $\equiv Si-O-Si\equiv \xrightarrow{+(RCO)_2O} 2\equiv Si-OCOR$,

(5) $\equiv Si-OR' \xrightarrow{+(RCO)_2O} \equiv Si-OCOR$,

(6) $\equiv Si-N< \xrightarrow{+RCOOH,\ (RCO)_2O} \equiv Si-OCOR$,

(7) $\equiv Si-S- \xrightarrow{+RCOOH,\ RCOOM,\ (RCO)_2O} \equiv Si-OCOR$,

(8) $\equiv Si-CN \xrightarrow{+RCOOM} \equiv Si-OCOR$,

(9) $\equiv Si-CNO \xrightarrow{+RCOOM} \equiv Si-OCOR$,

(10) $\equiv Si-CNS \xrightarrow{+RCOOM} \equiv Si-OCOR$,

(11) $\equiv Si-COOH \xrightarrow{\text{heat to } 190^\circ} \equiv Si-OCOH$,

(12) $\equiv Si-OCOR' \xrightarrow{RCOOH,\ (RCO)_2O} \equiv Si-OCOR$,

(13) $\equiv Si(OCOR)_2 \xrightarrow{R'OH} \equiv Si(OCOR)(OR')$.

The best methods for the synthesis of tetraacyloxy- and alkylacyloxysilanes are those based on the reaction of halogenosilanes with acids or their salts and anhydrides, but such methods cannot be used to prepare alkoxyacyloxy- or alkylalkoxyacyloxysilanes; these are most often prepared by methods such as the reaction of acid anhydrides with alkoxysilanes or of alcohols with acyloxysilanes.

The intermediate formation of (alkylthio)acyloxysilanes (which have not as yet been separated as individual compounds) is assumed in the reaction between tri(alkylthio)silanes and acetic anhydride to form thioesters (I):

$$HSi(SR)_3 + (CH_3CO)_2O \longrightarrow CH_3COSR + [CH_3COOSiH(SR)_2], \qquad (I)$$

$$[CH_3COOSiH(SR)_2] \longrightarrow CH_3COSR + \left(-O-\underset{\underset{SR}{|}}{\overset{\overset{H}{|}}{Si}}-\right)_x. \qquad (II)$$

Wolinski et al.[111] assume the formation of the unstable second reaction product di(alkylthio)acetoxysilane (I), which then decomposes according to Eqn. (II) to give a thioester and an organosilicon polymer.

II. REACTIONS OF ACYLOXYSILANES

1. Reactions of Tetraacyloxysilanes

Tetraacyloxysilanes are liquid (propionyloxy[39] and butyryloxy[41]), amorphous (formyloxy[28]), or crystalline (acetoxy[1,42], benzoyloxy[40,51], trichloracetoxy, stearoyloxy, naphthoyloxy, and others[41]). They are soluble in inert organic solvents such as benzene, acetone, and ether, and are very hygroscopic. On heating they decompose to acid anhydride and silica:

$$Si(OCOR)_4 \longrightarrow 2(RCO)_2O + SiO_2.$$

Tetraacetoxysilane decomposes at 160°–170°[1], but in a vacuum (5–6 mm Hg) it sublimes without noticeable decomposition at 148°. Tetrakis(monochloroacetoxy)silane decomposes even at 50°–60° (6 mm Hg), while tetraformyloxysilane cannot be obtained pure, since it always contains silica. This decomposition reaction is the basis for the preparation of the anhydrides of acetic[112] (yields 75–96%), propionic[113], and butyric (yield 76.6%[26]) acids.

Tetraacyloxysilanes derived from saturated monobasic acids are hydrolysed instantaneously; tetrabenzoyloxysilane reacts with water somewhat more slowly[40]. According to Khaskin[114,115] the hydrolysis of tetraacetoxysilane by the action of water containing labelled oxygen takes place predominantly by the following reaction, indicating the stability of the $\geqslant Si-O$ bond:

$$\geqslant SiO-COCH_3 + H\dot{O}-H \longrightarrow \geqslant SiO-H + CH_3CO-\dot{O}H.$$

Tetraacyloxysilanes react vigorously with alcohols; two different reaction schemes have been proposed. According to Friedel and Ladenburg's results[1], esters and silicic acid are formed (III), while Malatesta[51] considers that the products are organic acids and tetraalkoxysilanes (IV):

$$Si(OCOR)_4 + 4R'OH \longrightarrow 4RCOOR' + Si(OH)_4, \quad (III)$$

$$Si(OCOR)_4 + 4R'OH \longrightarrow Si(OR')_4 + 4RCOOH. \quad (IV)$$

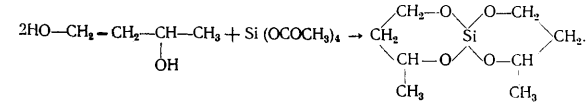
It has been found recently[110] that even in the cold, tetraacetoxysilane reacts exothermically with primary and secondary alcohols, forming (depending on the ratios of reactants) tetraalkoxysilanes or alkoxyacetoxysilanes:

$$Si(OCOCH_3)_4 + xROH \rightleftarrows (CH_3COO)_{4-x}Si(OR)_x + xCH_3COOH \quad (V)$$

where $x = 1-4$.

These products are obtained smoothly only when the reactants are used in molar proportions and the resulting acetic acid is removed by distillation in a vacuum. If the acetic acid is distilled at normal pressure or the reaction mixture is first heated, the yield of alkoxy derivatives falls sharply, and the alkyl acetate and a gel of silicon polymer are obtained. These experimental results were explained as follows: above 80°–90° reaction (V) may become reversible, and the acetoxysilane acetylates the alcohol, forming the acetate; the ester is formed by esterification of the alcohol with acetic acid, the $(CH_3COO)_{4-x}Si(OR)_x$ acting as water-removing agent. It must be added that tertiary alcohols react with much more difficulty than primary and secondary, reaction only taking place on heating to 100°–140°; for example, not more than three acetoxy groups can be replaced by t-butoxy groups.

The reaction of tetraacetoxysilane with 1,3-butandiol produces in good yield the spirocyclic orthosilicic acid ester 4,8-dimethyl-1,5,7,11-tetraoxa-6-silaspiro[5,5]undecane[116]:



Contrary to this reaction, 1,4-butandiol and 1,5-pentandiol gave only the acetates[116]:

$$2HO-[CH_2]_n-OH + Si(OCOCH_3)_4 \rightarrow 2CH_3COO-[CH_2]_n-OCOCH_3 + Si(OH)_4 \quad (n = 4-5).$$

Tetraacetoxysilane reacts with dry ammonia to form acetamide and silicic acid[1,117]:

$$Si(OCOCH_3)_4 + 4NH_3 \rightarrow 4CH_3CONH_2 + Si(OH)_4.$$

Yur'ev, Belyakova, and coworkers showed that the acylation of ethyl-, diethyl-, and dibutylamine with tetraacyloxysilanes derived from saturated monobasic organic acids is a convenient method for the preparation of *N*-alkyl and *N*,*N*-dialkyl acid amides (yields 60–90%)[54,117,118]:

$$4R'R''NH + Si(OCOR)_4 \rightarrow 4RCONR'R'' + Si(OH)_4;$$

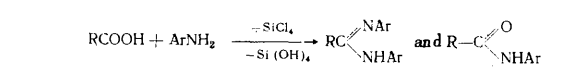
(1) $R' = H$; $R'' = C_2H_5$; $R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9, n-C_5H_{11};

(2) $R' = R'' = C_2H_5$; $R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9, n-C_5H_{11};

(3) $R' = R'' = C_4H_9$; $R = CH_3$, C_2H_5, n-C_3H_7, n-C_5H_{11}.

N,*N*-diethylamides of aromatic acids (benzoic, *o*- and *p*-toluic) are obtained in lower yields (24–63%). The reduced acylating power of aromatic tetraacyloxysilanes is due to the greater strength of these acids[117]. The reaction of tetraacetoxy- and tetrabenzoyloxysilanes with aniline and methylaniline has given the corresponding anilides[51,118]; however, in the reaction of the monochloroacetoxysilane with aniline, only the molecular compound of composition $ClCH_2COOH \cdot C_6H_5NH_2$ has been separated[51].

The arylamides of various monobasic acids (including hydroxy- and amino-acids) have been obtained by reacting the corresponding acids with silicon tetrachloride and the arylamine. Acyloxysilanes are apparently intermediates in this reaction; in the case of 2,3-hydroxynaphthoic acid a yellow polymeric substance of composition $[(OCOC_{10}H_6O)_2Si]_x$ was separated. If the reaction is carried out in excess silicon tetrachloride, diarylamidines are obtained in 50–79% yield, often together with the arylamides[119,120]:



Acylation of phenyl- and acetylhydrazine with the tetraacyloxysilanes derived from monobasic organic acids gives the corresponding acid phenyl- and acetylhydrazides (yields 61–85%)[54,117]:

$$4R'NHNH_2 + Si(OCOR)_4 \rightarrow 4R'NHNHCOR + Si(OH)_4$$

where R' = C_6H_5 or CH_3CO.

Yur'ev and Belyakova obtained only the mono-*N*,*N*-diethylamide of succinic acid in the acylation of diethylamine with tetrasuccinyloxysilane, thus convincingly confirming the structural formula suggested for the acyloxysilanes derived from dibasic acids, in which each of the four acid

residues contains a free carboxyl group[32]:

$$(HOOC[CH_2]_2COO)_4Si + 4NH(C_2H_5)_2 \xrightarrow{-Si(OH)_4} 4HOOC(CH_2)_2CON(C_2H_5)_2.$$

Like the anhydrides of organic acids, the tetraacyloxysilanes can acylate phenols, and can acylate the benzene nucleus in the Friedel–Crafts reaction. Thus in 1947 Petrov and Itkina[121] used tetrabutyryloxysilane as the acylating agent for the preparation of phenyl butyrate:

$$Si(OCOC_3H_7)_4 + 4C_6H_5OH \xrightarrow{70°} 4C_3H_7COOC_6H_5 + Si(OH)_4.$$

These workers were the first to condense tetrabutyryloxysilane with benzene and toluene in the presence of aluminium chloride to obtain propyl phenyl ketone (in low yield) and propyl-*p*-tolyl ketone (37% yield) respectively:

$$Si(OCOC_3H_7)_4 + 4\,C_6H_5R \xrightarrow{AlCl_3} 4\,C_3H_7CO{-}C_6H_4R + Si(OH)_4,$$

where R = H or CH_3.

Somewhat later, Petrov and Lagucheva[29] carried out analogous condensations of other tetraacyloxysilanes with benzene, toluene, and chlorobenzene, and obtained the following ketones: benzophenone (58% yield), a mixture of phenyl *o*-tolyl and phenyl *p*-tolyl ketones (86%), methyl *p*-tolyl ketone (62.7%), methyl *p*-chlorophenyl ketone (45.4%), and acetophenone (47%). Tetraformyloxysilane has also been used to acylate phenol and toluene[28]; the yield of phenyl formate reached 46%, but the yield of *p*-tolualdehyde was very low, the reaction product consisting mainly of crystalline substances which are further conversion products of the *p*-tolualdehyde. According to Petrov and Lagucheva's results[29], the pure tetraacyloxysilane, separated from the solvent in which it was prepared, had a lower acylating power than the same acyloxysilane when used in solution in the solvent without separation; however, it was later shown by other workers that this is incorrect.

Yur'ev, Elyakov, and coworkers in 1952 studied the acylation with tetraacyloxysilanes of the five-membered heterocyclic compounds furan and thiophene[122–124] and selenophene[125,126]. In the presence of anhydrous stannic chloride in benzene, there were obtained methyl-2-furyl ketone (7% yield), and ketones of the thiophene (53–96% yields) and selenophene (62–82% yields) series:

$$4\,C_4H_3X + Si(OCOR)_4 \rightarrow 4\,C_4H_2X{-}COR + Si(OH)_4,$$

where X = O, R = CH_3;

X = S, R = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, s-C_4H_9, t-C_4H_9, n-C_5H_{11}, n-C_7H_{15}, n-$C_{15}H_{31}$, n-$C_{17}H_{35}$, C_5H_9, C_6H_{11}, C_6H_5, or $C_{10}H_{11}$;

X = Se, R = C_2H_5, s-C_4H_9, n-C_4H_9, C_5H_9, C_6H_5.

The yields of 2-thienyl ketones decrease as branching of the carbon chain increases. A peculiarity of acylation with tetraacyloxysilanes is the need to employ equimolar or even greater quantities of catalyst (as in acylation with acid chlorides), whereas with acid anhydrides catalytically small quantities are used. A detailed study of the acetylation of thiophene and benzene with tetraacetoxysilane in the presence of various condensation agents[127] has shown that in the acetylation of thiophene in the presence of titanium tetrachloride, with a molar ratio of catalyst to acetic acid of 0.4 : 1, the yield of acetylthienone at 60° was 37%, and with a ratio of 0.83 : 1 reached 93.5%*; tetraacetoxysilane, which acetylates thiophene in the presence of anhydrous $BeCl_2$, $ZnCl_2$, $BF_3 \cdot (C_2H_5)_2O$, and $TiCl_4$, does not acetylate benzene under the same conditions; the acetylating agent is the acetoxysilane itself; in activity in the acylation of the aromatic nucleus, tetraacyloxysilanes occupy the last place in the series acid chloride > acid anhydride > tetraacyloxysilane; the acylation of thiophene with tetraacetoxysilane prepared in benzene and not isolated from it, and with pure tetraacetoxysilane, give identical results under identical conditions in benzene in the presence of stannic chloride as catalyst.

Yur'ev and Elyakov acylated the pyrrole nucleus by heating pyrrole with a tetraacyloxysilane derived from a saturated monobasic acid (after removal of the solvent in a vacuum) at 180° in the presence of anhydrous sodium acetate; ketones of the pyrrole series were obtained in yields of 34–56%[128]:

$$4\,C_4H_4NH + Si(OCOR)_4 \xrightarrow{CH_3COONa} 4\,C_4H_3NH{-}COR + Si(OH)_4.$$

In the acylation of indole in the presence of stannic chloride, the yield of 3-acetylindole did not exceed 21%, with respect to reacted indole[128].

Unsaturated monobasic organic acids (vinylacetic, allylacetic, Δ^3-cyclohexenecarboxylic) also react with silicon tetrachloride to form the corresponding tetraacyloxysilanes, which on condensation with benzene (in the presence of aluminium chloride), thiophene, and selenophene (in the presence of stannic chloride) give the corresponding unsaturated ketones, although in low yields (20–30%) because of much resinification. When acylating benzene, the reaction is also complicated by alkylation of the benzene by the resulting unsaturated ketone[129].

The tetraacyloxysilanes derived from saturated dibasic organic acids are prepared by reacting silicon tetrachloride with the acids in benzene, and, as indicated above, have a free carboxyl group on each of the four acid residues attached to the silicon atom; therefore, as Yur'ev, Elyakov, and Belyakova showed, they acylate benzene in the presence of aluminium chloride to form ω-benzoylalkanoic acids (yields 51–96%)[48]; in the acylation of thiophene in nitrobenzene in the presence of aluminium chloride, ω-(2-thenoyl)alkanoic acids are obtained in 33–77% yields. In neither case were diketones detected. These tetraacyloxysilanes do not acylate thiophene in benzene in the presence of stannic chloride[130].

Selenophene was acylated with tetrasuccinyloxysilane at -30° in a mixture of nitrobenzene and carbon disulphide in the presence of aluminium chloride, but the yield of β-2-selenoyl)propionic acid was only 7%[49]:

$$4\,C_4H_4X + Si(OCO[CH_2]_n{-}COOH)_4 \xrightarrow[-Si(OH)_4]{AlCl_3} 4\,C_4H_3X{-}CO(CH_2)_n{-}COOH,$$

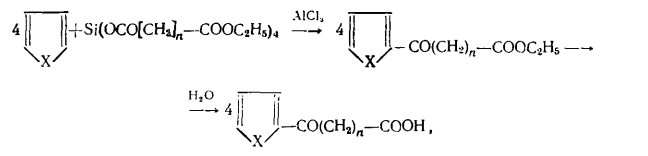
where X = S or Se.

* The quantity of catalyst and yield of ketones were calculated with respect to the acid used in the preparation of the tetraacyloxysilane.

The same workers showed that the tetraacyloxysilanes derived from the ethyl half-esters of dibasic acids acylate benzene (in the presence of aluminium chloride) and thiophene and selenophene (in the presence of stannic chloride). For example, the acylation of benzene with the acyloxysilane derived from monoethyl malonate gave ethyl benzoylacetate in 33% yield[48]:

$$4C_6H_6+Si(OCOCH_2COOC_2H_5)_4 \longrightarrow 4C_6H_5COCH_2COOC_2H_5+Si(OH)_4 .$$

The acylation of thiophene and selenophene with the acyloxysilanes derived from the monoethyl esters of dibasic acids, with subsequent hydrolysis of the resulting keto-acid esters, gave δ-(2-thenoyl)valeric acid (66% yield) and ω-(2-selenoyl)-alkanoic acids (20–42% yields)[49]:



where X = S or Se.

Yur'ev, Belyakova, and Volkov showed that the tetraacyloxysilanes derived from α-halogeno saturated organic acids have lower acylating activity than the corresponding unsubstituted compounds, and can only be used in acylation reactions in the presence of strong condensation agents such as aluminium chloride. On the basis of the acylation of benzene with the compounds derived from acetic, monochloro-, dichloro-, and trichloroacetic acids, it was shown that the greater the strength of the acid, the lower the acylating activity of its derivative. The acylation of benzene with tetra(β-bromopropionyloxy)silane produces, depending on the conditions, either β-bromopropiophenone (70% yield) or a mixture of β-hydroxy- and β-phenylpropiophenone[30]. Tetra(β-chloropropionyloxy)silane and tetra(γ-chlorobutyryloxy)silane only exhibit strong alkylating properties[131].

The acylation of benzene and, particularly, five-membered heterocyclic rings, with tetraacyloxysilanes has a number of advantages over methods of acylation using acid chlorides or anhydrides; the tetraacyloxysilanes can be used in the solvent in which they are prepared, and so are more readily available than the acid chlorides and anhydrides, particularly those with branched chains or of high molecular weight. Also, the slightly lower reactivity of the tetraacyloxysilanes is very valuable in the acylation of heterocyclic compounds of clearly aromatic nature; the acylation of selenophene with the tetraacyloxysilanes derived from monobasic acids and the monoethyl esters of dibasic acids is the most convenient method for the preparation of ketones and keto-acids of the selenophene series. Nesmeyanov, Perevalova, and coworkers[132], using tetraacetoxysilane to acetylate ferrocene, obtained the monoacetyl derivative, while acetyl chloride gave the diacetyl derivative of ferrocene.

Yur'ev and Belyakova have shown that tetraacyloxysilanes can successfully replace acid anhydrides in the acylation of compounds with a labile hydrogen atom, such as malonic and acetoacetic esters. The acylation of malonic ester[54,133,134] in the presence of magnesium oxide and copper acetate at 165°–170° produces symmetrical β-diketones of the type $RCOCH_2COR$, in yields of 34–37%:

$$CH_2(COOC_2H_5)_2+Si(OCOR)_4 \xrightarrow{-Si(OH)_4} 2(RCO)_2C(COOC_2H_5)_2 \xrightarrow[-C_2H_5OH,\ -CO_2]{+H_2O} 2RCOCH_2COR,$$

where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9, and n-C_5H_{11}.

The acylation of acetoacetic ester under the same conditions and with subsequent ketonic dissociation produces unsymmetrical β-diketones of the type CH_3COCH_2COR in yields of 34.5–77%[54,133,134]:

$$4CH_3COCH_2COOC_2H_5+Si(OCOR)_4 \xrightarrow[-C_2H_5OH\ -CO_2]{+H_2O} 4CH_3COCH_2COR.$$

where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, and iso-C_4H_9.

The ability of tetraacyloxysilanes derived from saturated monobasic acids to acylate acetylene in the presence of aluminium chloride[135] is of great interest. The reaction apparently passes through an intermediate stage in which there is addition to the triple bond to form an ester of orthosilicic acid and a β-hydroxyvinyl alkyl ketone, which then dissociates to give a β-chlorovinyl alkyl ketone:

$$Si(OCOR)_4+CH{\equiv}CH \xrightarrow{AlCl_3} [Si(OCH{=}CHCOR)_4] \xrightarrow{AlCl_3} 4RCOCH{=}CHCl+Si(OAlCl_2)_4,$$

where R = CH_3, C_2H_5, n-C_3H_7, and n-C_5H_{11}.

An important property of tetraacyloxysilanes is the lability of the hydrogen atoms in the α-methylene group. Khaskin[136] studied the possible replacement of the hydrogen atoms in tetraacetoxysilane by deuterium, and found that in the presence of sodium acetate this exchange takes place to the extent of 92% in 25 h:

$$Si(OCOCH_3)_4+4CH_3COOD \longrightarrow Si(OCOCH_2D)_4+4CH_3COOH.$$

Because of the lability of the hydrogen atoms in the α-methylene groups, the condensation of tetraacetoxysilane with benzaldehyde by the Perkin reaction in the presence of sodium acetate takes place (although more slowly than the isotope exchange) even at 100°, which is too low a temperature for the condensation of benzaldehyde with lead acetate and acetic anhydride[114,136].

The condensation of tetraacyloxysilanes with aromatic aldehydes, furfural, and thiophene-2-aldehyde in the presence of salts of the corresponding acid or of potassium carbonate was studied in detail by Yur'ev, Elyakov, and Vysokosov, who obtained cinnamic acid (74.5% yield)[137], its homologues (22–69.5%)[138] and derivatives (36–89.5%)[139], and also furyl-2-acrylic acid and its homologues (26–70.5%) and thienyl-2-acrylic acid (80%)[140]:

$$2RCHO+Si(OCOCH_2R')_4 \xrightarrow{-Si(OH)_4} 2RCH{=}\underset{\displaystyle R'}{\overset{\displaystyle |}{C}}{-}COOH+2R'CH_2COOH.$$

The reaction of tetraacyloxysilanes with organomagnesium compounds had not been studied until recently; only in 1953–54 did Lanning describe the reactions between tetrapropionyloxysilane and ethylmagnesium bromide[39], and tetrabenzoyloxysilane and phenylmagnesium bromide[40]. According to his results, the products are triethylcarbinol and triphenylcarbinol respectively, and an unidentified silicon-containing compound. Lanning and Moore[41] reported in 1958 that they had isolated tertiary alcohols (in 56–59% yield) and an ethylsiloxane fraction of general formula $[(C_2H_5)_2SiO]_x$, where x = 3 or 4, from the reaction product of tetraacyloxysilanes with ethylmagnesium bromide. If the reaction is carried out with 80% of the required quantity of Grignard reagent, ketones (26–29%) can also be isolated, in addition to the tertiary alcohols (42–45%).

Yur'ev and Belyakova showed that the main products of the reaction between tetraacetoxysilane and alkylmagnesium halides (on longer boiling of the reaction mixture) are

tertiary alcohols (58–68.5% yields) and tetraalkylsilanes (51–72%), with higher-boiling fractions which are apparently siloxanes[141]:

$$Si(OCOCH_3)_4 + 12RMgX \longrightarrow 4CH_3R_2COH + SiR_4,$$

where R = CH_3, C_2H_5, n-C_3H_7, and n-C_5H_{11}.

The reaction of tetraacetoxysilanes with organocadmium compounds produces ketones in 20–46% yields[141]. The reaction is apparently as follows:

$$Si(OCOCH_3)_4 + 4RCdX \longrightarrow 4RCOCH_3 + Si(OCdX)_4.$$

2. Reactions of Acyloxytrichlorosilanes

Acyloxytrichlorosilanes are colourless, mobile, very hygroscopic liquids which fume strongly in air. They disproportionate ("symmetrise") relatively easily into silicon tetrachloride and tetraacyloxysilanes:

$$4RCOOSiCl_3 \longrightarrow 3SiCl_4 + Si(OCOR)_4.$$

Those derived from *o*-chloro- and *o*-nitrobenzoic acids are completely disproportionated in 1 h, and those derived from *p*-toluic and benzoic acids in a month. All acyloxytrichlorosilanes disproportionate when distilled, some partially, others completely. The tendency of the fatty acid derivatives to disproportionate decreases with increase in the length of the carbon chain and with increase in the degree of branching in the chain. This tendency increases with increasing strength of the acid. Disproportionation is also favoured by reduced pressure, increased temperature, and small amounts of the starting acid[53,54,56].

Acyloxytrichlorosilanes are active acylating agents for aromatic compounds (benzene, thiophene)[142]. The yields of ketones when benzene is acylated are considerably higher than when acylating with tetraacyloxysilanes. For instance, the yields of substituted benzophenones (70–88%) are as good as those obtained in the acylation of benzene with substituted benzoyl chlorides.

The yields of the corresponding ketones in the acylation of thiophene with acyloxytrichlorosilanes in the presence of stannic chloride, as when tetraacyloxysilanes are used, are 60–95%[55,142].

The acyloxy group in the acyloxytrichlorosilanes is highly reactive; the action of 1 mole of anhydrous ethyl alcohol at -30° substitutes an ethoxy group for the acyloxy group more easily than for the chlorine atom, and the acid is obtained in 66–72% yield, possibly as a result of the catalytic influence of the hydrogen chloride liberated in the partial replacement of the chlorine atom by the alkoxy group. The reaction of acyloxytrichlorosilanes with acids produces mixed anhydrides of silicic acid and the two different organic acids[55,56]:

$$RCOOSiCl_3 + 3R'COOH \longrightarrow RCOOSi(OCOR')_3 + 3HCl.$$

With organomagnesium compounds, acyloxytrichlorosilanes behave similarly to tetraacyloxysilanes, forming tertiary alcohols (74–89% yields) and tetraalkylsilanes (53–72% yields)[55,56].

3. Reactions of Alkyl-, Alkylalkoxy-, and Alkoxyacyloxysilanes

Alkylacyloxysilanes are solids or liquids with a pleasant ethereal smell[73], unstable to heating. Thus methylphenyldiacetoxysilane decomposes on heating to 200° into acetic anhydride and polymethylphenylsiloxane[82]:

$$xCH_3(C_6H_5)Si(OCOCH_3)_2 \longrightarrow x(CH_3CO)_2O + [CH_3(C_6H_5)SiO]_x.$$

Triphenylacetoxysilane decomposes on distillation in a vacuum (3 mm Hg)[75], but triphenylformyloxysilane is stable to heating to 180°[60]. Characteristic of unsymmetrical alkylacyloxy- and alkoxyacyloxysilanes, as with all organosilicon compounds, is their ability to disproportionate on heating to form symmetrical molecules[101], e.g.:

$$2CH_3COOSi(OC_2H_5)_3 \longrightarrow (CH_3COO)_2Si(OC_2H_5)_2 + Si(OC_2H_5)_4.$$

Alkylacyloxysilanes are hydrolysed with varying degrees of ease; the most easily hydrolysed are alkyltriacetoxysilanes[7,80,82]; dialkyldiacyloxysilanes are hydrolysed almost as easily[7,79,88]. The hydrolysis products are mainly polysiloxanes.

Trialkylacyloxysilanes are hydrolysed by water with considerably more difficulty[58,90,98], with the exception of those prepared from dibasic acids[58].

According to Larsson's results, alkylalkoxyacyloxysilanes are hydrolysed much more rapidly in a homogeneous medium, and in the presence of ammonia, sodium carbonate, and caustic potash[143].

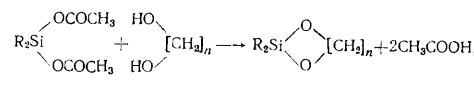
Andrianov and coworkers and Dolgov and coworkers showed that when alkylacetoxysilanes react with alcohols, an alkoxy group replaces the acetoxy group, with the liberation of acetic acid[69,72,81,109]:

$$R_xSi(OCOCH_3)_{4-x+y}R'OH \longrightarrow R_xSi(OCOCH_3)_{4-x-y}(OR')_y + yCH_3COOH.$$

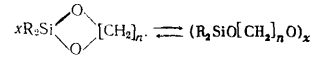
Tertiary alcohols react with more difficulty than primary and secondary alcohols[69].

Andrianov and Dubrovina studied the reaction of alkylacetoxysilanes with glycidol and showed that as the number of acetoxy groups in the silane decreases, it becomes more difficult to replace them by glycidol residues, and, for example, trimethylacetoxysilane does not undergo substitution in this way[72].

Davydova, Voronkov, and Dolgov established that the reaction between dialkyldiacetoxysilanes and β-, γ-, δ-, and ε-glycols produces cyclic ethers of dialkylsilanediols containing 6-, 7-, 8-, and 9-membered rings in 50–70% yields:



where n = 3–6. The reaction is accomplished by mixing the reagents and distilling off the resulting acetic acid in a vacuum. If the acid is distilled at atmospheric pressure, the main reaction product is the glycol acetate. The residue after the vacuum distillation is a polymer, and only after thermal depolymerisation (by sublimation in a vacuum), accompanied by rearrangement of the Si–O–C bonds, is the expected cyclic ether formed. The depolymerisation is reversible, and on standing the cyclic ethers again polymerise:



Attempts to obtain five-membered cyclic ethers by reacting dimethyldiacetoxysilane with ethylene and propylene glycols produced in both cases dimers containing the 1,3,6,8-tetraoxa-2,7-disilacyclodecane ring[116,144].

Davydova, Voronkov, and Dolgov also established that dialkyldiacetoxysilanes react smoothly with pentaerythritol to form spirocyclic ethers of dialkylsilanediols:

$$2R_2Si(OCOCH_3)_2+(HOCH_2)_2C(CH_2OH)_2 \longrightarrow$$

$$\longrightarrow R_2Si\begin{matrix}O-CH_2\\O-CH_2\end{matrix}C\begin{matrix}CH_2-O\\CH_2-O\end{matrix}SiR_2+4CH_3COOH.$$

The reaction of dialkyldiacetoxysilanes with glycerol did not produce derivatives of the type

$$R_2Si\begin{matrix}O-CH_2\\O-CH_2\end{matrix}CHOH;$$

with R = C_2H_5, a compound was obtained of formula $C_{18}H_{40}O_6Si_3$; with R = CH_3, the product had the composition $C_7H_{18}O_5Si$, and contained two hydroxy groups and one acetoxy group; one of the hydroxy groups was attached to the silicon atom[116,145].

As mentioned above, the reaction of alkylacyloxysilanes with acids[76,77,100] is the basis of Anderson's method for the synthesis of alkylacyloxysilanes derived from acids of low volatility. Anderson[75] and Andrianov and coworkers[146] showed that with acid chlorides and with phosphorus tribromide[75], alkylacyloxysilanes give alkylhalogenosilanes:

$$R_xSi(OCOR')_{4-x}+(4-x)R''COCl \longrightarrow R_xSiCl_{4-x}+(4-x)R'COOCOR'',$$

$$3(CH_3)_3SiOCOCH_2Cl+PBr_3 \longrightarrow 3(CH_3)_3SiBr+P(OCOCH_2Cl)_3.$$

Only one instance of the reaction of alkylacyloxysilanes with a Grignard reagent has been studied. Methyldibutylcarbinol was prepared by the action of trimethylacetoxysilane on butylmagnesium bromide; no silicon-containing product was isolated[61].

Henglein and Schmulder[97] and Andrianov and coworkers[146] showed that diacyloxysilanes react with di- and trialkoxysilanes[97,146], phenyltrichlorosilane[146], and esters of boric acid[147] to form poly-organosiloxanes and poly-organoborosiloxanes respectively.

In his study of the exchange reactions of alkylacyloxysilanes with silver oxide and salts Anderson established that the acyloxysilanes do not react with silver iodide, chloride, bromide, sulphide, isocyanate, or isothiocyanate, react to a slight extent with silver cyanide, and better with silver fluoride, silver oxide, and the silver salts of organic acids[77].

Heating alkylacyloxysilanes with zinc and aluminium chlorides produces the corresponding alkylchlorosilanes[148,149].

According to Bradley and Thomas[150], the reaction of trialkylacetoxysilanes with alkoxy derivatives of titanium, zirconium, and tantalum can be used to prepare the trialkylsiloxy derivatives of these metals:

$$nR_3SiOCOCH_3+M(OR')_n \longrightarrow nR'OCOCH_3+M(OSiR_3)_n.$$

However, Andrianov and Ganina[151] showed that trimethylacetoxysilane and titanium tetrabutoxide do not react in this way, but produce a mixture of octaacetoxycyclotetratitanoxane, $[TiO(OCOCH_3)_2]_4$, and heptaacetoxytrimethylsiloxycyclotetratitanoxane, $[(CH_3COO)_2TiO]_3OTi(OCOCH_3)\cdot OSi(CH_3)_3$.

The main reaction is therefore replacement of butoxy groups by acetoxy groups. The reaction between trimethylacetoxysilane and titanium tetrachloride similarly takes place with exchange of chlorine for acetoxy groups, with the formation of cyclic polymers. The formation of compounds containing the Si–O–Ti group takes place with difficulty.

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POLYMERISATION OF ISOBUTENE

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INTRODUCTION

As is well known, much attention is now being paid to development of the chemical industry in this country, and in particular to production of high polymers, plastics, synthetic rubbers, and fibres. Products from the processing of gas and petroleum must form the basic raw materials for this new growth of the chemical industry.

In recent years processes for polymerising and copolymerising unsaturated compounds, particularly alkenes (ethylene, its homologues, and derivatives), have become important. The study of alkene polymerisation is based on the work of Russian and Soviet chemists, in the first place that of A. M. Butlerov. Both in the USSR and elsewhere the industrial utilisation of alkene-polymerisation processes for industrial gases has been under investigation for some decades; useful catalysts have been sought and prepared, and reaction mechanisms studied. It has been found that various acids (sulphuric, phosphoric, and hydrofluoric), natural and artificial aluminosilicates, halides of certain elements (aluminium, boron, zinc, titanium, tin, etc.), and individual metal oxides, are catalysts for polymerising the simplest alkenes to produce liquid products (motor spirits and viscous oils). More recently the polymerisation of alkenes to macromolecular solid polymers (polythene, polypropylene) has acquired great theoretical and practical interest. This can take place at ultra-high pressures in the presence of initiators (oxygen, organic peroxides), and also at atmospheric or elevated pressures in the presence of catalysts (metal oxides, organic aluminium compounds and titanium tetrachloride).

Of the alkene monomers used in industrial polymerisation processes, special interest attaches to isobutene, ethylene, and propene. Isobutene is a relatively accessible substance, which polymerises to a number of valuable products, superior in some respects to similar products obtained from other alkenes. Among these may be mentioned the isomeric isooctenes which are hydrogenated to isooctane (valuable as a petrol additive), high-quality lubricating oils, synthetic rubbers, and plastics.

The present article is a review of literature and patent information on isobutene polymerisation. Catalytic polymerisation of isobutene is of great practical importance and particular attention is given to it.

I. POLYMERISATION OF ISOBUTENE BY HEAT, FREE RADICALS, AND OTHER ACTIVE PARTICLES

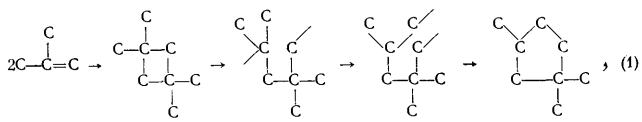
1. Action of Heat

It has been shown that isobutene[1] and t-butanol[2] decompose at dark-red heat, giving complex mixtures of products. According to Ipat'ev[3] polymerisation of isobutene in an iron tube at 380°–390°, with an initial pressure of 70 atm, leads to formation of a mixture of liquid saturated, unsaturated, and naphthenic hydrocarbons.

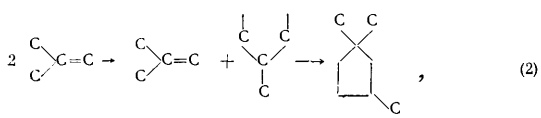
Hurd and Spence[4] considered that thermal activation of C–C and C–H bonds in isobutene leads to formation of univalent radicals, which further change into gaseous products, while activation of the C=C double bond leads to formation of diradicals $(CH_3)_2-\dot{C}-\dot{C}H_2$, giving rise to cyclohexane derivatives and to aromatic hydrocarbons derived from them. Gapon[5] put forward a similar hypothesis of formation of diradicals from alkenes by thermal activation.

According to Lebedev and Koblyanskii[6], when liquid isobutene was heated at 200° and 30 atm in a carbon dioxide atmosphere in sealed refractory glass tubes for 14 days, 6–8% of it polymerised, exclusively to triisobutene. Thermal polymerisation of isobutene in sealed tubes at ~370° is a homogeneous second-order reaction[7] with an activation energy of 43 kcal/mole.

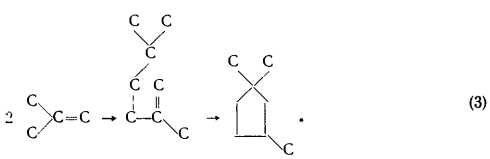
At 370°–460° and 36–360 atm isobutene[8] undergoes cyclodimerisation, the reaction-product (1,1,3-trimethylcyclopentane) yield being raised by increasing the time of heating or the highest pressure attained. A heating time of 1 h at 400°, pressure 36 atm, gave a liquid polymer with the highest content of dimer (49.5%). The gaseous reaction products, comprising ~4 wt.% of the reacted isobutene, contained isobutane, propane, propene, and traces of methane, in addition to isobutene. 1,1,3-trimethylcyclopentane was also obtained by thermal dimerisation of isobutene using a diluent (nitrogen)[9]. It has been suggested[8] that cyclodimerisation can take place by one of the following routes:



(1)

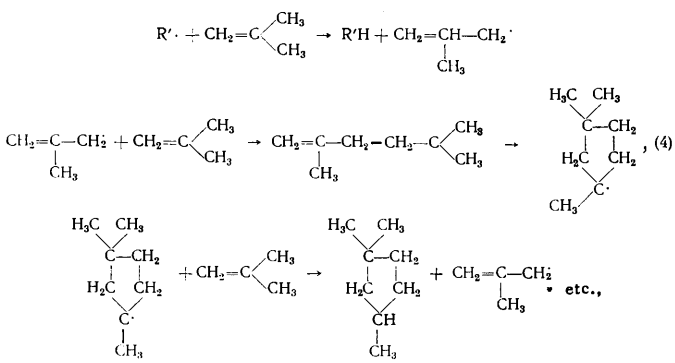


(2)



(3)

The last reaction scheme is the most probable one; it involves a radical chain mechanism, and can be depicted thus:



(4)

Stepukhovich and Mitenkov[11] described an interesting case of thermal polymerisation of isobutene. They studied its low pressure cracking at 811°–828°K and 2 mm Hg, when, instead of a pressure increase due to isobutene decomposition, there was an appreciable pressure drop (up to 20%). Apparently there was absorption of molecules of isobutene on the walls of the quartz reactor, and then heterogeneous catalytic polymerisation of isobutene took place at those parts of the walls covered by the absorbed molecules, polymerisation at first prevailing over cracking.

2. Action of α-Particles

Polymerisation of isobutene by α-particles has been little studied. Mund and coworker[12,13] found that this process has a negative temperature coefficient. The reaction rate can be represented by the semi-empirical equation

$$1/P = 1/P_0 + k(1 - e^{-\lambda t}) - k'(1 - e^{-at-bt^2}), \quad (6)^*$$

where P_0 is the initial pressure, P the pressure at time t, λ the radioactive (decay) constant for radon (0.0075), and a, b, k, and k' are constants. At 0° and 31°, 22 and 55 molecules respectively of isobutene were polymerised per ion. The authors ascribed the rapid drop in polymerisation rate with rise in temperature, not to change in the number of chains, but to change in their length. A small amount of hydrogen was formed, and the mean molecular weight of the polymer was ~4000. When isobutene was polymerised by α-particles at constant pressure (400–700 mm Hg at 0°), the ion yield was 33.6–46.2, and the mean molecular weight of the resultant polymer was 400–700.[14] The authors believed that the first stage of the process proceeds as follows:

$$\begin{aligned} &\text{1)}\ C_4H_8 \xrightarrow{\alpha\text{-particle}} C_4H_8^+ + e, \\ &\text{2)}\ C_4H_8^+ + e \rightarrow C_4H_7 + H, \\ &\text{3)}\ H + C_4H_8 \rightarrow C_4H_7 + H_2. \end{aligned} \quad (7)$$

3. Action of Radicals Formed by Photolysis of Aldehydes and Ketones

The rate of photolysis of the simplest aldehydes and ketones at 300° is decreased by admixture with alkenes[15]. Under these conditions the alkene is polymerised by each light quantum absorbed by the carbonyl compound, and the rate of polymerisation is independent of alkene pressure. Polymers of low molecular weight are formed, isobutene giving a dimer. The equations for the process are:

$$\begin{aligned} &CH_3CHO + h\nu = CH_3 + CHO, \\ &CH_3 + CH_3CHO = CH_4 + CO, \\ &CH_3 + CH_3 = C_2H_6, \\ &CH_3 + C_nH_{2n} = R_1, \\ &R_1 + C_nH_{2n} = R_2, \\ &R_{n-1} + C_nH_{2n} = R_n. \end{aligned} \quad (8)$$

It was assumed that chain breaking was due to isomerisation of a large radical into a species of low reactivity.

4. Electric Discharges

Electric discharges act on alkenes, and more specifically, on isobutene, in various ways, depending on the nature of the discharge. An arc discharge, like high temperatures, causes profound decomposition of isobutene

* Eqn. (5) is missing from Russian text (Ed. of Translation).

molecules, while the silent discharge brings about polymerisation[16], as first observed by Dem'yanov and Pryanishnikov[17]. The experiments were carried out in an ozoniser, in which a discharge occurred at various alternating currents, the potential difference being 12–13 kV. A yellowish oil was obtained, average molecular weight 140, consisting mainly of diisobutenes and triisobutenes, but containing a small amount of a hydrocarbon C_5H_8. The authors[17] advanced a hypothesis that the silent discharge not only opens the alkene double bond, leading to polymerisation, but also splits off radicals. Pryanishnikov[18] made a more detailed investigation of polymerisation of isobutene by the silent electric discharge. The light fractions of the liquid polymerisation product contained 70–80% of saturated and 20–30% of unsaturated hydrocarbons, while in the high-boiling fractions the ratio was reversed (40 : 60). Polymerisation was accompanied by splitting off and addition of radicals, as was shown by the presence of C_6 and C_7 hydrocarbons (2,2-dimethylbutane and 2,2-dimethylbutene, 2,4- and 2,2-dimethylpentanes, and 2,2,3--trimethyl butane and the corresponding alkenes). Naphthenes were also present in the high-boiling fractions. Isomura[19] observed the formation of a liquid product of mean molecular weight 152 and consisting mainly of three fractions: 80°–85°, 100°–110°, and 190°–200°. Otto and Müller-Cunradi[20] obtained lubricating-oil additives by polymerising isobutene in the silent electric discharge.

5. Action of Peroxides and Other Substances Giving Free Radicals

Little attention has been paid to the polymerisation of isobutene in the presence of substances which can decompose to give free radicals. The existing patent literature describes mainly processes for copolymerising isobutene with other unsaturated compounds to obtain macromolecular substances of the synthetic-rubber type. Among the substances which have been copolymerised with isobutene are alkenes, alkadienes, styrene[21], aldehydes, and ketones having an α-hydrogen atom[22,23], and C_2F_4.[24] The following can be used as initiators: benzoyl peroxide[22]; dialkyl peroxides[25]; organic polyperoxides[26]; hexachloroethane, $(NH_4)_2S_2O_8$; $N_2H_4 \cdot 2HCl$, $NH_2OH \cdot HCl$[23]; $R_3C(CR_2)_nR$, where R can be phenyl or substituted phenyl but not hydrogen[21,27]; imino compounds of the type $RR'C=NA$, where R and R' are hydrogen or hydrocarbon radicals, and A is H, OH, NH_2, or $N=CR''R'''$; nitro derivatives of hydrocarbons[28]; and also substances giving diradicals on homolysis[29]. Copolymerisation takes place over a wide temperature range (-164° to 550°, depending on the initiator used), and at pressures up to 3000 atm.

Polymerisation is sometimes carried out in emulsions using peroxide catalysts plus emulsifiers. It then takes place at much lower temperatures and is characterised by a higher reaction rate. The literature does not describe polymerisation of pure isobutene in aqueous emulsion. Usually it is copolymerised with other unsaturated compounds, e.g. fumaric esters[30-32], acrylonitrile, methyl methacrylate, vinyl acetate, unsymmetrical dichloroethylene, methyl chloroacrylate, styrene[33], and vinyl halides[33,34]. The aqueous emulsion must have pH 3–8.5. The process is carried out at 50°–100° in the presence of potassium persulphate, H_2O_2, and similar materials[30], with added emulsifiers, usually sodium or potassium stearate.

Isobutene has also been copolymerised with acrynonitrile in suspension in a medium in which only the initiator, and not the starting materials or final product, was soluble. The mixtures contained up to 85% of acrylonitrile[35].

II. CATALYTIC POLYMERISATION OF ISOBUTENE

1. Acid-Catalysed Polymerisation

Sulphuric acid. Butlerov and Goryainov[36,37] first described the polymerisation of isobutene by sulphuric acid. When isobutene was absorbed in sulphuric acid ($H_2SO_4 : H_2O = 3 : 1$) a quantity of oil always accompanied the t-butanol formed. Half of this oil was triisobutene, but it also contained a small amount of higher polymers. When isobutene was passed into strong sulphuric acid, it was all converted to triisobutene plus higher polymers[38]. Dimerisation was observed with much diluted acid[39].

Diisobutene is obtained by dissolving 1 volume of liquid isobutene in 2 volumes of concentrated H_2SO_4 which has been diluted with an equal volume of water, and then heating in sealed tubes to 100°. Diisobutene can also readily be obtained by heating a mixture of dilute H_2SO_4 and t-butanol[38]. According to Butlerov[40], isobutene cannot be dimerised directly to diisobutene, but only through t-butanol as an intermediate, the latter forming diisobutene when heated at 100° with dilute H_2SO_4. At ordinary temperature, without the hydration stage, the trimer immediately results, and when concentrated H_2SO_4 is used, higher polymers are also obtained.

By passing isobutene through aqueous sulphuric acid (5 : 1), Lebedev and Koblyanskii[6] obtained a product containing 1% diisobutene, 90% triisobutene, and 9% polyisobutenes. Butlerov's trimer contained two isomers: 90% of a low-boiling one and 10% of a high-boiling one.

In the copolymerisation of isobutene with n-butenes in the presence of sulphuric acid to obtain isooctane[41], 60–75% H_2SO_4 selectively absorbs isobutene in the cold. A temperature of 20°–40° is required to obtain an appreciable increase in polymerisation rate. Raising the temperature to 100° doubles the polymer yield. The dimer is the main product when isobutene alone is polymerised by 70% sulphuric acid at 20°.

Katsuno[42] showed that if the sulphuric acid concentration is below 77%, the isobutene polymerisation product consists mainly of dimer and trimer. Lowering the acid concentration and raising the temperature raises the yield of dimer. With 58% H_2SO_4 at 68°–71° the dimer yield was a maximum (70%). The dilute acid absorbs isobutene slowly. Higher acid concentration and lower temperature favour a higher degree of polymerisation.

Isobutene was rapidly absorbed by 77% H_2SO_4 at room temperature, to give a 70% yield of trimer consisting of 2,2,4,6,6-pentamethylhept-3-ene, 2,2-dimethyl-4-neopentylpent-3-ene, and 2,2-dimethyl-4-neopentylpent-4-ene, in the ratios 1 : 2 : 1*. When the temperature was lowered below 20°, 67% sulphuric acid did not cause polymerisation, but there was absorption with formation of t-butanol. However, when this mixture was kept at 70°–100°, polymerisation occurred, and part of the isobutene was regenerated. By previously diluting the mixture with water,

* This account follows Chem. Abs., 43, 5176 (1949) (ref. 42), but 2,2-dimethyl-4-neopentylpent-3-ene is the same as 2,2,4,6,6-pentamethylhept-3-ene (Ed. of Translation).

the rate of polymerisation could be lowered and the yield of dimer raised. The product of slow polymerisation at room temperature was mainly trimer. The di- and triisobutenes formed can undergo secondary changes in the presence of sulphuric acid.

The polymerisation of isobutene is reversible, and low temperatures favour shift of equilibrium in the direction of polymer formation. At 100° equilibrium is shifted towards the trimer. The temperature for polymerisation of isobutene by H_2SO_4 can be lowered to 0° [43], but then the acid concentration must not be less than 85–90%. At 0° there is 85% conversion of isobutene to liquid polymers.

According to Nametkin[44], the polymerisation of alkenes by concentrated sulphuric acid, gives both unsaturated polymers and also saturated hydropolymers; the appearance of the latter implies that hydrocarbons more unsaturated than the alkenes are formed. This process, called hydro-dehydropolymerisation, occurs readily with isobutene, a series of hydropolymers being formed, from hydrodimer to hydrohexamer and higher:

$$\begin{gathered} H_2SO_4 + C_4H_8 \longrightarrow HOSO_2OC_4H_9 \xrightarrow{C_4H_8} H_2SO_4 + C_8H_{16}, \\ C_8H_{16} + C_4H_9OSO_2OH \longrightarrow C_8H_{18} + HOSO_2OC_4H_7, \\ nC_4H_7OSO_2OH \longrightarrow (C_4H_6)_n + nH_2SO_4. \end{gathered} \quad (9)^*$$

Many workers[38,45-53] have investigated the structures of the isobutene polymers formed by the action of sulphuric acid. It has been found that the dimer consists of 2,4,4-trimethylpent-1-ene and 2,4,4-trimethylpent-2-ene in the ratio of 4 : 1.

Investigation of the trimeric fraction of the isobutene polymers[40,54-59] showed that it contained 2,2,4,6,6-pentamethylhept-3-ene, 4,4-dimethyl-2-neopentylpent-1-ene, 2,4,4,6,6-pentamethylhept-1-ene, and 2,4,4,6,6-pentamethylhept-2-ene.

In the light of the results obtained[59] the following reactions can be postulated. A proton, H^+, plus an isobutene molecule form a carbonium ion:

$$(CH_3)_2C{=}CH_2 + H^+ \rightleftarrows \underset{(I)}{(CH_3)_3C^+}. \quad (12)$$

The carbonium ion (I), like a proton, adds to an isobutene molecule giving the carbonium ion (II):

$$(CH_3)_3C^+ + CH_2{=}C(CH_3)_2 \rightleftarrows \underset{(II)}{(CH_3)_3CCH_2C^+(CH_3)_2}, \quad (13)$$

which can, with loss of H^+ from the methylene group or from a methyl group, give the two isomers of diisobutene:

$$(CH_3)_3CCH_2C^+(CH_3)_2 \rightleftarrows \begin{cases} (CH_3)_3CCH_2{-}\underset{\displaystyle CH_3}{\overset{}{C}}{=}CH_2 + H^+ \\ (CH_3)_3CCH{=}C(CH_3)_2 + H^+. \end{cases} \quad (14)$$

The formation of mainly 2,4,4-trimethylpent-1-ene can be explained by the proton splitting off more readily from a methyl group attached to the electron-deficient carbon atom, than from the neopentyl group.

When diisobutene adds H^+, it gives the carbonium ion (II). Similarly it can add the carbonium ion (I). But addition of (I) to β-diisobutene does not occur, since formation of 2,4,4-trimethyl-3-t-butylpent-2-ene has not been observed. The union of (I) with α-diisobutene can be depicted thus:

$$(CH_3)_3C^+ + CH_2{=}C(CH_3)CH_2C(CH_3)_3 \rightleftarrows \underset{(III)}{(CH_3)_3CCH_2C^+(CH_3)CH_2C(CH_3)_3}. \quad (15)$$

(III) splits off a proton, either from the adjacent methylene group or from a methyl group:

$$(III) \rightleftarrows \begin{cases} (CH_3)_3CCH_2{-}\underset{\displaystyle CH_2}{\overset{}{C}}CH_2C(CH_3)_3 + H^+ \ (54\%) \\ (CH_3)_3CCH{=}\underset{\displaystyle CH_3}{\overset{}{C}}CH_2C(CH_3)_3 + H^+ \ (36\%). \end{cases} \quad (16)$$

The ion (II) can also add to isobutene:

$$(CH_3)_3CCH_2C^+(CH_3)_2 + CH_2{=}C(CH_3)_2 \rightleftarrows \underset{(IV)}{(CH_3)_3CCH_2C(CH_3)_2CH_2C^+(CH_3)_2}. \quad (17)$$

The ion (IV), losing a proton, gives the trimers:

$$(IV) \rightleftarrows \left.\begin{array}{l} (CH_3)_3CCH_2C(CH_3)_2CH_2\underset{\displaystyle CH_3}{\overset{}{C}}{=}CH_2 + H^+ \\ (CH_3)_3CCH_2C(CH_3)_2CH{=}C(CH_3)_2 + H^+ \end{array}\right\} 10\% \quad (18)$$

Phosphoric acid. Of all acids, phosphoric acid and its salts are the most widely used for alkene polymerisation. The acid is usually employed in the liquid form, or as the "solid" acid, or as copper pyrophosphate. Sometimes phosphorus pentoxide is used.

When isobutene, n-butenes, or ethylene is slowly passed over P_2O_5 spread on pumice, there is complete gas absorption at room temperature, after an induction period of a few hours[60]. When the catalyst saturated with gas is heated to 110°, pure dimerised isobutene boils off. With a reaction temperature above 110°, trimer and tetramer are found in the products.

According to Ipat'ev and Corson[61,62], isobutene at atmospheric pressure is polymerised much faster by liquid orthophosphoric acid than n-butenes, and the presence of isobutene accelerates the polymerisation of but-1-ene. Mixtures of isobutene and n-butenes polymerise at lower temperatures and at lower acid concentrations than the n-butenes alone, a mixture of alkenes being formed.

Mild polymerisation conditions favour formation of the simpler polymerisation products, e.g. the isobutene polymers formed at 30° contained only two components, diisobutene and triisobutene, whereas the polymers formed at 130° contained seven compounds. 100% orthophosphoric acid is a more powerful polymerisation catalyst than the 95%, 89%, and 85% acids; pyrophosphoric acid on pumice[63] is more active than metaphosphoric acid.

A comparative study of the polymerisation of isobutene by sulphuric and orthophosphoric acids showed[64] that at 110° and atmospheric pressure the concentration of H_2SO_4 must not exceed 65%; if it does, profound decomposition of the reaction product is observed. Under the same conditions 87–100% orthophosphoric acid was more active, and the activity was enhanced by addition of 4–5% H_2SO_4. Addition of over 10% H_2SO_4 favoured decomposition of the reaction products.

With pumice impregnated with 87–100% H_3PO_4, isobutene at 30°–150° was converted to a product comprising 55–60% of dimer and 25–30% of trimer. When the temperature was raised above 30°, the rate of polymerisation first increased, passed through a maximum, and then, because of depolymerisation, fell. With 87% H_3PO_4 the optimum temperature was 110°, and for 100% acid it was 130°.

With P_2O_5 on pumice the contraction of the gas was very great at the beginning of reaction, then it rapidly decreased, and afterwards became steady. When the temperature was

* Eqns. (10) and (11) are missing from the Russian text (Ed. of Translation).

raised, the contraction diminished, but this happened at lower temperatures than with H_3PO_4 on pumice.

One catalyst, active charcoal containing up to 76% H_3PO_4, was 5–6 times as active for polymerising isobutane at 50°–55° as liquid orthophosphoric acid[65]. When reaction was effected with a layer of catalyst (4–5 mm), the polymers contained up to 53% of dimeric material. Decreasing contact time decreased the formation of high polymers, but did not affect the yield of trimeric isobutene.

The acid phosphate of iron, $Fe(H_2PO_4)_3$, deposited on charcoal, caused (in a 10 mm layer) reaction at 50°–60° under a pressure of 10–30 atm[66]. Reaction took place to the extent of 5–7%, dimer being formed. The catalyst was unstable because of hydrolysis of the salt and leaching out of the acid. A more stable catalyst, $Fe(H_2PO_4)_3 \cdot 2H_2O$, contained excess phosphoric acid and gave a product containing up to 80% of dimer. Raising the temperature to 105°–110° led mainly to the formation of trimers. Moisture in the starting material, while increasing the rate of polymerisation, particularly at 100°–105°, decreased the amount of dimer in the polymers and caused a rapid fall in catalyst activity. A catalyst of composition $FeH_3(PO_4)_2 \cdot 2.5H_2O$ was somewhat less active than the one just described, and gave up to 66% of dimer.

Hydrogen fluoride. Polymerisation of isobutene by hydrogen fluoride[67–69] takes place at ordinary or enhanced temperature under slight pressure. But side reactions leading to fluorination and destruction of the polymers also occur, particularly at elevated temperatures.

Fluorophosphoric acids. Topchiev and Andronov[70] showed that mono- and difluorophosphoric acids and their molecular compounds with BF_3 can be active catalysts for polymerising isobutene. Silica gel and activated carbon were used as supports for them. The nature of the support and the contact time had a considerable effect on the extent of polymerisation.

Polymerisation took place at 15°–152° and atmospheric pressure. As the temperature was raised, the degree of polymerisation fell and the yields of dimeric and trimeric fractions rose. Higher temperatures favoured isomerisation; in addition to 2,4,4-trimethylpent-1-ene and -2-ene, the dimer contained isomeric octenes, such as 2,3,4-trimethylpent-2-ene. When silica gel was used, the polymers were more volatile than with carbon, but the polymer yield was considerably less. The carbon-supported catalyst was the more stable. The order of catalytic activity was:

$$HPO_3 \cdot BF_3 > H_3PO_4 \cdot BF_3 > HPO_2F_2 > H_2PO_3F.$$

Dihydroxyfluoroboric acid. This was used[71] as a catalyst for copolymerising isobutene with propene or n-butenes at 0°–40° and 3–8 atm. The polymers were hydrogenated; the product from isobutene and propene contained 67% of heptanes, 95% being 2,3-dimethylpentane. The yield of the C_8 fraction from hydrogenated isobutene–but-1-ene copolymer was ~43%, and it contained 34% of dimethylhexanes and 66% of trimethylpentanes. In the same way the yield of the C_8 fraction from hydrogenated isobutene–but-2-ene copolymer was 36%, and it consisted wholly of trimethylpentanes.

Sulphonic Acids. C_1–C_4 sulphonic acids are effective catalysts above 60°. At lower temperatures they react with alkenes to give stable esters[72]. Polymerisation can be carried out in two ways: (1) by preparing the ester and then heating it at 60°–120° with free acid, in which case there is an induction period of up to 60 min; (2) by passing the alkene at atmospheric pressure into the acid heated to a temperature high enough for polymerisation to take place without intermediate formation of esters. Isobutene is readily polymerised even at room temperature, trimer being the main product.

The patent literature mentions trichloroacetic acid and hexanoic acid[73] as isobutene polymerisation catalysts.

The following conclusions can be drawn from this review of the acid polymerisation of isobutene and from the amounts and structures of the polymers formed: Isobutene is usually acid-polymerised at 0°–300°, and as the temperature is raised side reactions are accelerated. For example, with H_3PO_4 the products of polymerisation at 100° are just polymers; at 100°–300° depolymerisation products accompany the polymers, while above 300° saturated and naphthenic hydrocarbons are formed.

With sulphuric acid, the temperature range for forming solely polymers of the starting alkene is much less, but it is hard to define it precisely, since not only temperature, but also the acid concentration and the pressure have great influence on isobutene polymerisation.

When hydrofluoric acid is used as catalyst, it brings about polymerisation of the isobutene accompanied by formation of products of various molecular weights which are not actually polymers.

The mechanism of acid polymerisation, with particular reference to ethylene and propene, has been discussed in a paper[75] to which one of the present authors contributed. The schemes to which most attention should be paid are those involving intermediate formation of esters[61,62] and one which involves assumed C–C or C–H scission giving rise to a methyl group plus an alkene radical or to a hydrogen atom plus an alkene radical, which initiate polymerisation by adding to the alkene double bond[76]. Lately, however, a scheme put forward by Whitmore[77] (and discussed above), involving carbonium ions, has gained widespread acceptance. Many authors have discussed this mechanism in detail; among other things it is assumed that polymerisation involving carbonium ions is a chain reaction[10,74,78].

2. Halide-Catalysed Polymerisation

Metal halides. The course of polymerisation of the lower alkenes — in particular isobutene — by metal halides depends to a considerable extent on the reaction temperature. At 0°–200° liquid products are usually formed, consisting mainly of dimers and trimers of the starting alkene. At -80° to -160° the so-called low temperature polymerisation of alkenes occurs; it is of great practical importance because it results in high-molecular-weight polymers[79]. This process, brought about by catalysts of the Gustavson–Friedel–Crafts type, usually takes place in the liquid phase with a diluent which is either inert or else forms a complex with the catalyst. The amount of catalyst is usually ~0.1% of the isobutene. Low temperature polymerisation of isobutene[80,81] is a chain reaction and takes place with almost explosive speed. Rubber-like solid polymers of molecular weight over 100 000 can be obtained in quantitative yields.

The molecular weight of the polymer increases when the temperature is lowered from -20° to -100°. Thus when isobutene is polymerised at its boiling point an oily polymer is formed after a considerable induction period, but

at -80° a solid polymer is formed without any induction period.

Addition of other alkenes, e.g. n-butenes, to the isobutane lowers the yield and the molecular weight of the polyisobutene; this reduction is very marked when diisobutene or triisobutene are added. This shows that though polymerisation must proceed in successive stages, the dimer and trimer are not intermediates, a view which is further supported by the fact that di- and triisobutenes, which undergo slow polymerisation to oils at room temperature, do not give macromolecular products at low temperatures.

Alcohols and ethers, e.g. diethyl ether[82], have, like alkenes and alkadienes, a retarding effect on the reaction.

Beryllium halides. Polymerisation of isobutene in the presence of $BeCl_2$,[83,84] at 200° and initial pressure 27 atm, affords an 80% yield of hydrocarbons; 80% of the liquid hydrocarbons are a benzine fraction comprising mainly diisobutene and isomeric hydrocarbons plus triisobutene and its isomers. A tetramer occurs in the high-boiling fraction, and in the low-boiling material there are isopentane, isohexane, and isohexene. The gaseous products are: propene, n-butenes, and unchanged isobutene.

When reaction is carried out using $BeCl_2$ in sealed glass tubes, more than half of the polymerisate is a viscous oil. The difference in the way in which reaction takes place indicates additional catalysis by the walls of the reactor. BeF_2 is a less active catalyst than $BeCl_2$.

Zinc chloride. The tendency of isobutene to be polymerised by $ZnCl_2$ at room temperature has long been known. According to Kondakov[85], reaction of isobutene with zinc chloride in sealed tubes gave a solid crystalline product and a liquid mixture consisting of diisobutene and t-butyl chloride, taken to be an intermediate reaction product. Polymerisation of isobutene at room temperature took place relatively slowly, the main reaction products being diisobutene, octyl chloride, and an insignificant quantity of trimer. The reaction rate increased appreciably when the temperature was raised or the amount of zinc chloride was increased, di-, tri-, and tetraisobutenes being obtained. The resultant polymers were identical with the polymers obtained by Butlerov's method employing sulphuric acid.

Even prior to Kondakov, it was shown[86,87] that isobutanol is changed into a mixture of polyisobutenes (mainly di- and triisobutenes) under the influence of zinc chloride. Addition of HCl accelerates the reaction, which becomes almost explosive: a violent evolution of gas, consisting mainly of isobutene and isobutane, occurs. Petrov et al.[88] investigated the conversion of isobutanol to polyisobutenes at 300°–330°, both at atmospheric pressure and at elevated pressure, and showed that under pressure the yield of diisobutene could be doubled and the catalyst consumption diminished 12-fold. The authors also showed that 2,2,4- and 2,2,3-trimethylpentenes were present in the dimeric material.

Isobutene is not polymerised by $ZnCl_2$ in a copper tube at 600°.[89]

Zinc chloride can be used as a catalyst for copolymerisating isobutene with alkadienes to obtain solid polymers[90].

Boron fluoride and its derivatives. Butlerov and Goryainov[37] reported that alkenes could polymerise in the presence of BF_3. Topchiev and coworkers[91] made a detailed investigation of the polymerisation of isobutene by BF_3 and its derivatives; it was 90–95% polymerised in the liquid or vapour phase in the presence of 1–2% of boron trifluoride etherate deposited on a solid carrier, to give a product containing 20–26% of dimer, 65–75% of trimer, and quite a small amount of higher polymers[91]. The nature of the carrier (activated charcoal, pumice, silica gel, aluminium oxide, and copper turnings), and the temperature over the range 5°–130° did not affect the polymer yield or the ratio of dimer to trimer. Vapour-phase polymerisation of isobutene occurred most effectively at 5°, since at that temperature there was not such extensive loss of catalyst from the carrier as at higher temperatures. The structures of the dimer and trimer were elucidated, and a small amount of saturated hydrocarbon (which could have arisen through hydropolymerisation) was established[92].

The reaction of isobutene in the presence of BF_3 on platinum and on Cr_2O_3 catalysts at various temperatures has been studied in detail[93]. The catalysts used were platinum on activated carbon (Pt + C), Pt + C + BF_3, C + + BF_3, BF_3 + $Cr_2O_3 . Al_2O_3$, and $Cr_2O_3 . Al_2O_3$, at 250°–400° i.e. at temperatures considerably higher than those usually employed in polymerisation of alkenes by BF_3.[94]

With all these catalysts the degree of polymerisation and molecular weights of the products fall with increase in temperature, although the alkene conversion remains rather high. Platinum on carbon alone does not bring about polymerisation of isobutene; with Pt + C + BF_3 the conversion is 90%, and with C + BF_3 it is 65%. At 400° there was also hydropolymerisation and partial aromatisation.

Paushkin and Shcherbakova[95] investigated how the carrier affects the catalytic action of BF_3. Activated carbon and aluminosilicate, both with a 15–20% content of BF_3, were used as catalysts. The nature of the polymerisation both at room temperature and at 100°, as well as the effectiveness of the catalyst, depended on the carrier, though neither activated carbon nor aluminosilicate caused polymerisation of alkenes under the conditions employed.

Activated charcoal plus BF_3 brought about more profound polymerisation than aluminosilicate plus BF_3, or $Et_2O . BF_3$. This was ascribed to a difference in the mechanism of catalysis; in the case of BF_3 plus aluminosilicate, this is similar to the action of BF_3 plus phosphoric acid or BF_3 plus water, and is related to formation of more effective complex acids.

Topchiev and Alyavdina[96,97] showed that the molecular compounds of BF_3 with K_2SO_4 and Na_2SO_4 could be used to polymerise isobutene. When either the reaction temperature or the space velocity was raised, the degree of polymerisation fell. Similar behaviour was observed when silica gel + BF_3 was used as the catalyst, but at 150°, part of the BF_3 was lost from the silica gel surface. The dimeric portion of the polymerisate contained 2,4,4-trimethylpent-1-ene and -2-ene, as well as 3,4,4-trimethylpent-2-ene, and 2,3,4-trimethylpent-1-ene and -2-ene, which shows that isomerisation also takes place.

It is believed that the molecular compound of BF_3 with K_2SO_4 or Na_2SO_4 dissociates at high temperatures,

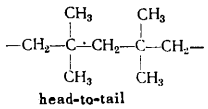
$$K_2SO_4 \cdot BF_3 \rightleftarrows K_2SO_4 + BF_3, \qquad (19)$$

and that the BF_3 liberated brings about the isobutene polymerisation.

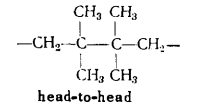
Evans, Polanyi, and coworkers[98] concluded that some third component must be present for rapid low temperature

polymerisation of isobutene in the presence of BF_3. When BF_3 was passed into unpurified isobutene polymerisation occurred very rapidly, but with carefully purified isobutene there was practically no polymerisation. It was concluded that this third component might be water, and support for this view was found when the reaction was carried out in the gas phase in a high vacuum[99]. The polymerisation took place only with impure isobutene containing water, and when the isobutene pressure exceeded a certain value. Purified isobutene polymerised rapidly if it was previously mixed with water vapour: 10^{-1} mm of water vapour was enough to initiate reaction. In addition to water, other effective initiators were t-butanol[100,101] and acetic acid[102]. The action of an activator was ascribed to complex formation with BF_3 and donation of a proton to the alkene, to form a carbonium ion, which initiated polymerisation. By introducing a separately-prepared BF_3-acetic acid complex, rapid polymerisation was brought about, and the authors assumed that it occurred on the surface of the crystals of the complex. Diethyl ether also functions as an activator, but is much less effective than t-butanol or acetic acid.

The product of low-temperature polymerisation of isobutene by BF_3 has a high molecular weight. The structure of a polymer molecule can vary according to the way in which the isobutene molecules are linked together:



head-to-tail (20a)

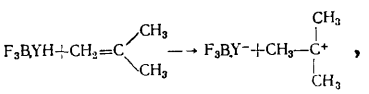


head-to-head (20b)

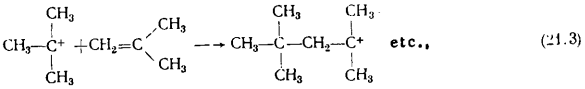
A mixed structure is also possible. Both chemical[81] and physical methods (X-ray analysis[103]) showed that the polyisobutene molecule actually has a head-to-tail structure. However, the authors of the paper referred to thought that the steric hindrance caused by the methyl groups made it necessary to twist successive isobutene units so that the methyl groups of one lay between two methyl groups of another; the molecules thus had a spiral configuration. But if a molecular model of polyisobutene corresponding to (20b) is constructed, no steric hindrance is found, and the molecule is unstrained. We may suppose that with any 1,1-disubstituted ethylene, including isobutene, the heat of formation of a polymer of type (20a) must be abnormally low because of steric hindrance. Calculation of the heat of formation of the hypothetical unstrained head-to-tail polyisobutene by various methods[100,103,104] gives 19.2–24 kcal/mole, which is much above the actual heat of formation of 12.8 kcal/mole[104]. The difference between the heats of formation of hypothetical and actual polyisobutene molecules must be ascribed to steric hindrance being overcome in the actual molecule.

Evans and Polanyi[100] put forward the following scheme for the low-temperature polymerisation of isobutene by BF_3:

$$BF_3+YH \longrightarrow F_3BYH, \qquad (21.1)$$



(21.2)



(21.3)

where YH is a compound containing mobile hydrogen. Stages (21.2) and (21.3) are analogous to the stages of the ionic mechanism advanced for the ordinary acid polymerisation of alkenes[77,105].

The affinity of an alkene molecule for a proton and for a carbonium ion increases on passing from ethylene to isobutene. The affinity is also greater for addition of a proton to the first C atom (methylene group) than it is for addition to the tertiary C atom, in agreement with Markovnikov's rule. Hence the authors[100] conclude that a tertiary carbonium ion will always participate in reaction (21.2). In chain propagation (21.3) the carbonium ion adds on so that the terminal group is always a tertiary one, and in this way the head-to-tail structure comes about. In addition to the ionic mechanism for this reaction, the authors consider the possibility of a radical one.

However, Houtman[106], who investigated the polymerisation of isobutene by BF_3 and $AlCl_3$, came to the conclusion that the presence of moisture, to act as activator, is not essential with these catalysts. A mechanism was advanced in which both π electrons of the alkene are fixed by the catalyst on one of the two carbon atoms joined by the double bond, so that a dipole is formed, and this, adding other monomer molecules, give a macromolecular product. Houtman allows Evans and Polanyi's[100,104] mechanism for formation of low-molecular-weight polymerisation products, but he considers that it is wrong to identify that mechanism with the low-temperature polymerisation one.

Dainton and Sutherland[107] considered that the mechanism for low-molecular-weight polymerisation of isobutene closely resembles that for the macromolecular one. From infra-red spectra, they demonstrated that the products of both reactions have $C(CH_3)_3$ and $-CH_2-C(CH_3)=CH_2$ as end groups, and they uphold the mechanism which Evans and Polanyi previously advanced[100].

Later Evans and coworkers[101,108] again confirmed that the presence of a third component (H_2O, t-butanol, acetic acid, or diethyl ether) is essential for both low- and high-temperature polymerisation of isobutene by BF_3. The third component forms stable complexes, and reaction takes place on the surface of crystals of the complex; in this respect there is no difference between high- and low-temperature polymerisation. Reaction can occur either via a carbonium ion, or via radicals. A carbonium ion is formed by addition of a proton from the catalyst complex to the alkene, and not by addition of the alkene to the catalyst.

But there are facts which indicate that the mechanisms of low- and high-temperature polymerisation of isobutene by BF_3 are not the same. For example, many substances, such as HCl, which facilitate high-temperature polymerisation (as mentioned above), retard low-temperature polymerisation[80,81].

Topchiev et al. showed[80] that the activity order for low-temperature polymerisation of isobutene by various BF_3 compounds in the absence of solvent was

$$BF_3>C_6H_5OCH_3\cdot BF_3>H_2O\cdot BF_3>H_3PO_4\cdot BF_3>(C_2H_5)_2O\cdot BF_3, \qquad (22)$$

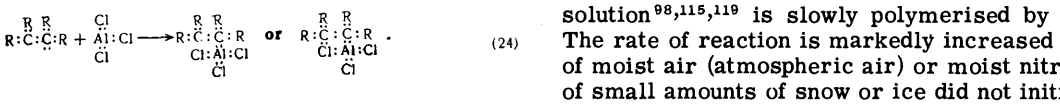
while for high-temperature polymerisation there is a different series[109]:

$$H_3PO_4\cdot BF_3>H_2O\cdot BF_3>H_2SO_4+BF_3>BF_3>RO\cdot BF_3. \qquad (23)$$

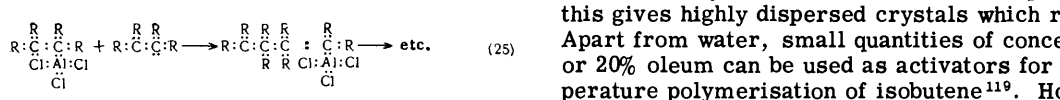
This difference is ascribed to there being different mechanisms for the stepwise polymerisation and the chain polymerisation of isobutene.

Aluminium chloride. Gustavson also used aluminium chloride as a polymerisation catalyst for alkenes[110]. Later[111] the polymerisation of isobutene by $AlCl_3$ at 100° and 150° was studied. A complex of the composition $(AlCl_3 \cdot C_4H_8)_n$ was obtained, together with a liquid polymerisate which contained paraffins and naphthenes in addition to alkenes. Isobutene is polymerised very violently by $AlCl_3$ [105], and reaction begins as soon as the gas comes into contact with the catalyst. Two layers are obtained; the upper one is a colourless oil of average molecular weight 200 and bromine number 10–15, and the lower one, a red viscous oil, is a complex containing 11.5% of aluminium. Further reaction of isobutene with this complex gave a quantitative yield of a colourless oil, and the aluminium content of the complex fell to 8.75%. If the isobutene and complex reacted at 140°, the final complex salt contained 10.5% of aluminium. Treatment of the complex with water afforded a yellowish oil, molecular weight ~270. Isobutene plus ether vapour reacted violently with $AlCl_3$, giving a viscous red oil containing ~12% of aluminium. Isobutene was not polymerised at room temperature or at 140° by the complex $Al_2Cl_6 \cdot 2C_6H_5N(CH_3)_2$, but polymerisation took place with $Al_2Cl_6 \cdot C_6H_5N(CH_3)_2$ and the composition of the complex changed until it became completely inactive, when it contained 10.48% Al and 2.63% N, corresponding to the composition $Al_2Cl_6 \cdot C_6H_5N(CH_3)_2 \cdot 2C_4H_8$.

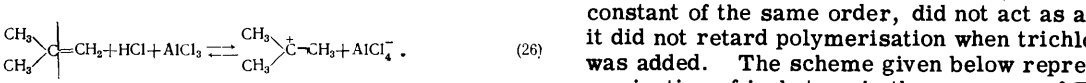
In metal halides of the aluminium chloride type the metal has an incomplete electron octet and can act as an electron acceptor. Aluminium usually has the coordination number 4 in the formation of aluminium chloride complexes, and it can add an electron pair from an active donor, e.g. from an alkene molecule. Polymerisation of alkenes by $AlCl_3$ can be depicted thus[105]:


(24)

The polymer chain grows by successive addition of an alkene molecule to this complex:


(25)

However, there is reason to doubt whether such compounds are active catalysts for the polymerisation of alkenes. As indicated above, boron trifluoride gains activity by the addition of an activator having mobile hydrogen in its molecule (water, acetic acid, etc.[101,112]). Other metal halides behave similarly in the presence of activators ($SnCl_4$, etc.[113]). So a number of authors assumed[98,99,112-116] that polymerisation of alkenes takes place only by reaction of metal halide with activator present. It is possible that the activator is a source of protons which, adding to the alkene molecule, give a carbonium ion. With aluminium chloride and HCl a carbonium ion can be formed by the reaction[78]


(26)

In the presence of water a proton can be given off by the complex formed from the catalyst and activator:

(27)

This complex is decomposed with formation of HCl, which is a proton source:

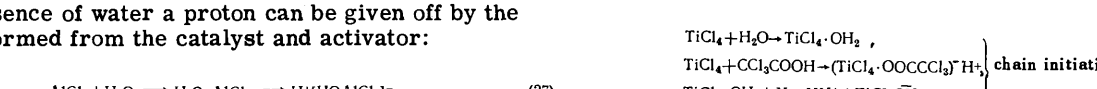

(28)

Other schemes have been put forward to explain the catalytic action of systems comprising catalyst and activator, in which the polymerisation is considered to be initiated by energy liberated by addition of activator to catalyst or processes involving hydro- or dehydrohalogenation are postulated. But these mechanisms are less probable than carbonium ion ones[114].

Low-temperature polymerisation of isobutene has been carried out in pentane solution in the presence of $AlCl_3$ [117] between -78° and 16°. Reaction started immediately and vigorously, yielding viscous products of varying molecular weight. The product of reaction at -35° to -40° was ~30% polymers, of molecular weight 280–616 and 50% polymers with molecular weights 3100–4800, and in the product obtained at 7°–16° ~60% had molecular weight 132–270, and 40% had molecular weight 358–686.

Vainshtein and Dintses[118] investigated the action of $AlCl_3$ between -70° and -10° on a cracking gas butane-butene fraction containing 15–30% of isobutene. To prevent the reaction from proceeding violently at the start, the catalyst was deactivated with dichloroethylene, carbon tetrachloride, heptene, or a solution of the butane-butene fraction polymers. The aluminium chloride complex was decomposed by treatment of the reaction products with alcohol at -30°. Reaction at -20° to -30° gave polymers suitable for addition to lubricating oils. The reaction rate increased with increasing $AlCl_3$ concentration over the range 0.15–1%, and thereafter remained constant. At -30° 90% of the isobutene was polymerised in an hour. When reaction temperature was increased from -70° to -10°, the molecular weight of the polymers fell correspondingly from 12 000 to 6000.

Titanium tetrachloride. Isobutene in n-hexane solution[98,115,119] is slowly polymerised by $TiCl_4$ at -90°. The rate of reaction is markedly increased by introduction of moist air (atmospheric air) or moist nitrogen. Addition of small amounts of snow or ice did not initiate reaction. Thus, with $TiCl_4$ an activator, probably water, is essential, but it can only be in the form of water vapour. Evidently this gives highly dispersed crystals which react with $TiCl_4$. Apart from water, small quantities of concentrated H_2SO_4 or 20% oleum can be used as activators for the low-temperature polymerisation of isobutene[119]. However, they cannot be used to study the reaction kinetics, because they form complexes with $TiCl_4$ which are insoluble in hexane. Substances which initiate liquid-phase polymerisation of isobutene by BF_3 at room temperature (acetic acid, diethyl ether), act as inhibitors in the case of $TiCl_4$. But dry trichloroacetic acid[119,120] is an effective activator; it forms the complex $TiCl_4 \cdot CCl_3COOH$ in hexane. In that case the polymerisation is a first order reaction with respect to CCl_3COOH. As the temperature is raised the reaction rate rises linearly, and the molecular weight of the polymers increases with increase of isobutene concentration and catalyst concentration. Picric acid, with a dissociation constant of the same order, did not act as an activator, but it did not retard polymerisation when trichloroacetic acid was added. The scheme given below represents the polymerisation of isobutene in the presence of $TiCl_4$:


(29.1) (29.1a) chain initiation (29.2)

$$MH^+ + M \rightarrow M_2H^+;\ M_2H^+ + (n-2)M \rightarrow M_nH^+,\ \text{chain growth} \quad (29.3)$$

$$\left.\begin{array}{l} M_nH^+ + TiCl_4OH^- \rightarrow M_n^- + TiCl_4 \cdot OH_2, \\ M_nH^+ + TiCl_4OH^- \rightarrow M_nHOH + TiCl_4, \end{array}\right\} \text{chain breaking} \quad (29.4),\ (29.4a)$$

$$M_nH^+ + M \rightarrow M_n + MH^+,\ \text{(reactive centre transfer)}, \quad (29.5)$$

where M is a monomer molecule.

This scheme is also typical of other metal halides. The most probable reaction for chain breaking is (29.4) and not (29.4a), because up to 2000 molecules of isobutene (in the case of BF_3 [121]) can polymerise for each molecule of water present.

Zirconium tetrachloride. Isagulyants and Bonkoi[122] investigated the polymerisation of isobutene by zirconium tetrachloride. At room temperature in the liquid phase (sealed tubes) reaction took place very readily, and oily polymers were formed regardless of the quantity of catalyst present. Increasing the amount of catalyst from 0.2% to 2% raised the polymer molecular weight from 638 to 1336. Isobutene conversion was a maximum with 1% of catalyst, when the polymer molecular weight was 900 and it contained 76–90% of unsaturated material. But when the catalyst concentration was raised to 27%, the quantity of unsaturated material dropped to 33%; this was ascribed to hydropolymerisation.

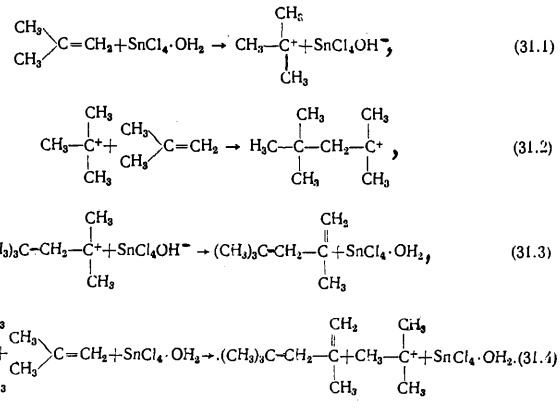
At 100°–200° and 10–70 atm reaction took place very readily with much evolution of heat. Complete conversion of isobutene with minimum catalyst consumption was obtained at 180°, when the resultant polymerisate, comprising almost wholly unsaturated hydrocarbons, boiled at 40°–340°. Diisobutene was the main product. Increasing the proportion of catalyst increased the yield of isomeric hydrocarbons. The dimeric material consisted mainly of 2,4,4-trimethylpent-1-ene (plus a small amount of the -2-ene), 2,3,4-trimethylpent-1-ene, 2,5-dimethylhex-2-ene, and 2,5-dimethylhex-3-ene. Wholly absent were 2,4,4-trimethylpentane, 2,5-dimethylhexane, and 2,3,4-trimethylpentane. A small amount of heavy hydrocarbons was found along with the diisobutenes.

Copolymerisation of isobutene with other alkenes using $ZrCl_4$ + HCl has been described[123].

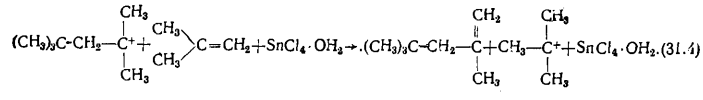
Stannic chloride. Investigation of the low-temperature polymerisation of isobutene by $SnCl_4$ [124] showed that at -78.5°, with C_2H_5Cl as a diluent, it is impossible to free the system from traces of water even with very careful purification. Polymerisation was very slow; the rate of polymerisation increased as the amount of water added was increased, up to a concentration of 0.5%, but the molecular weight of the polymer fell (from 57 200 at 0.056% H_2O to 51 000 at 0.688% H_2O). But $SnCl_4$ concentration and temperature also had major effects on polymerisation rate. With $SnCl_4$ concentration 1–2% the polymerisation rate was constant and independent of the catalyst concentration. Raising the temperature from -96.5° to -63.5° led to a 25-fold increase in reaction rate; the mean activation energy was 7 kcal/mole. Ethyl alcohol, t-butanol, diethyl ether, and acetone inhibited the reaction. The authors[124] considered that catalytic polymerisation at -78.5° could not occur in the absence of an activator for $SnCl_4$. Initiation of reaction does not consist simply of formation of a complex between stannic chloride and alkene. Apparently an equilibrium is established:

$$SnCl_4 + SnCl_4 \cdot 2H_2O \rightleftarrows 2SnCl_4 \cdot H_2O, \quad (30)$$

a hydrate able to initiate the process being formed. The low temperature polymerisation of isobutene in a solvent (ethyl chloride) can be represented as:



$$(CH_3)_3C{-}CH_2{-}C^+ + SnCl_4OH^- \rightarrow (CH_3)_3C{-}CH_2{-}C(=CH_2){-}CH_3 + SnCl_4 \cdot OH_2, \quad (31.3)$$



Hence the initial stage (31.1) of the reaction involves transfer of a proton from a molecule of hydrate to monomer. This can be thought of as involving, at the beginning, a complex with loosened bonds between the hydrate and the monomer. In solvents of low dielectric constant this complex can also exist as an ion pair. Chain growth can be stopped by reaction with a negative ion formed in the initial step [reaction (31.3)], or by proton transfer to monomer, giving rise to a new active centre.

Ferric chloride and bromide. Isobutene polymerisation and copolymerisation with alkenes and alkadienes have been effected in the presence of $FeCl_3$ plus accelerators (H_2SO_4, HNO_3, hexanoic and trichloroacetic acids)[125,126] and also in the presence of $FeBr_3$.[125]

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From the data given in the present section, it is evident that low-molecular-weight polymerisation, taking place above 0°, gives products similar to those obtained when mineral acids are used. Low-molecular-weight polymers are obtained — isobutene dimers, trimers, and tetramers. The reaction is complicated by the side reactions of isomerisation, cyclisation, and hydropolymerisation. Evidently polymerisation of isobutene by acids and metal halides at 0°–400° proceeds by one mechanism. The low-temperature polymerisation of isobutene to polyisobutene by metal halides, occurring below 0°, particularly at -70° to -120°, is very violent and takes place by a chain reaction. Reaction rate depends on catalyst activity. A comparative study of the activity of the catalysts was carried out in 1941–1942 by Fairbrother and Seymour; their results, given in a paper by Polanyi and coworkers[115], are set out in Tables 1 and 2. From these data it is evident that the

TABLE 1. Catalytic activity of metal halides. Initial temperature -78°.

Halide	Amount of catalyst, %	Amount of isobutene, %	Reaction time	Yield of polymer, %	Molecular weight $\times 10^{-3}$
BF_3	0.05	10	seconds	100	120—150
$AlBr_3$	0.05	20	1—5 min	70—90	120—150
$TiCl_4$	0.12—0.25	30	20—70 min	35—50	100—130
$TiBr_4$	1.0—1.5	30—50	12—18 h	30—50	70—90
BCl_3	0.9—1.5	40—50	12—18 h	0.5—1.5	30—50
BBr_3	0.6—1.0	50	12—18 h	0.5—1.5	20—30
$SnCl_4$	1.5—2.5	50	17—50 h	10—18	12—25

TABLE 2. Lower limit of concentration for polymerisation.

Catalyst		$AlBr_3$	$TiCl_4$	$TiBr_4$	BCl_3	$SnCl_4$
Composition of reaction mixture, %	isobutene	1.0	7.0	20	20	10
	catalyst	0.01	0.12	0.50	0.8	1.0

molecular weights of the polymers drop with decreasing activity of the metal halides, the degree of activity changing parallel to the acidity of the halide. In the presence of BF_3 polymerisation is completed in seconds with 100% conversion, with $AlBr_3$ it takes minutes and the conversion is 70–90%, while with $TiCl_4$ many hours are required and the yield is 35–50%. Finally, with $SnCl_4$ days are required, and the yield is 10–20%. Almost all the halides are activated by substances which as a rule have mobile H atoms; e.g. water, t-butanol, sulphuric, acetic, and trichloroacetic acid.

3. Polymerisation by Oxide Catalysts

Aluminosilicates. The polymerising action of aluminosilicates on alkenes was first established by Gurvich[127]. He observed that the unsaturated hydrocarbons present in petroleum lubricating oils, as well as pentene and pinene, were polymerised at room temperature, by a mildly calcined aluminosilicate — floridin. The activity of floridin was a maximum when the water loss was 12–13%, which occurs when it is heated to about 300°.

Lebedev and Filonenko[128] studied polymerisation of isobutene at room temperature in the presence of a floridin whose composition was 55.3% SiO_2, 21% Al_2O_3 + Fe_2O_3, 4.3% MgO + CaO, 1.9% K_2O + Na_2O, and 17.9% H_2O. On heating in air at 275°–325°, the floridin lost 12–12.3% of its moisture, and acquired an increased activity. Polymerisation of isobutene over floridin was also observed by van Winkle[129].

Lebedev and Koblyanskii[6] activated floridin at ~300° for 2 h. Isobutene was polymerised more energetically at -80° than at room temperature, and gave products of high molecular weight. At 200° polymerisation took place with difficulty, and at 290° it was not observed at all. Depolymerisation occurred over floridin at temperatures higher than room temperature, and with triisobutene this was already in evidence at 70°. Increase of contact time increased the yield of high polymers. Gaseous isobutene gave a product containing 18% of dimer, 51% of trimer, and 31% of higher polymers — tetramer, pentamer, and higher. The product obtained by polymerising liquid isobutene over floridin in sealed tubes for 3–24 h contained 4% of dimer, 25% of trimer, and 71% of higher polymers. The dimer, which was identical with Butlerov's diisobutene, was completely polymerised by floridin. The trimer did not polymerise under these conditions, and the pentamer was completely decomposed by floridin at 200° into dimer and trimer. The authors suggested that polymerisation proceeds stepwise according to the scheme

$$C_4H_8+C_4H_8 \longrightarrow (C_4H_8)_2 \xrightarrow[(C_4H_8)_2]{C_4H_8} \begin{matrix}\nearrow (C_4H_8)_3 \xrightarrow{(C_4H_8)_3} (C_4H_8)_5 \\ \searrow (C_4H_8)_4\end{matrix} \quad \text{etc.}, \qquad (32)$$

In view of the inertness of triisobutene and higher polymers to floridin, polymerisation involves only monomer and dimer.

Investigation of the depolymerisation of triisobutene[130] and higher polymers[131,132] by floridin showed that polymerisation of isobutene by that catalyst is reversible. According to Dobronravov and Frost[133] the equilibrium constant for

$$2\ \text{iso-}C_4H_8 \rightleftarrows C_8H_{16}\ \text{(diisobutene)}, \qquad (33)$$

over the temperature range 168°–313°, can be represented by the following semiempirical equation:

$$\log K' = \log \frac{p^2_{C_4H_8}}{p_{C_8H_{16}}} = -\frac{2959}{T} + 6.049 \pm 0.067\ . \qquad (34)$$

Polymers of different molecular weight were depolymerised[130–132] with varying ease. Diisobutene was the most stable: as the molecular weight increased, depolymerisation took place with great facility, forming monomer and dimer. Depolymerisation occurred at an appreciable rate even at 50°, and proceeded readily at 50°–250°. At the same time side reactions were observed: polymerisation of the monomer and dimer formed in the reaction, and, to some extent, hydrogen disproportionation leading to hydrocarbons more unsaturated than alkenes, along with saturated hydrocarbons. Triisobutene was 99% depolymerised, giving diisobutene and 0.5–1% of C_8H_{14} hydrocarbons plus isobutene.

When rubber-like polymers of isobutene were thermally degraded, monomer plus polymers ranging from dimer to pentamer were the sole products. At the same time saturated hydrocarbons, and C_n hydrocarbons, where n was not a multiple of 4, were formed.

Lebedev and Borgman[134] investigated in detail the conditions which were particularly favourable for obtaining high-molecular-weight polymers. Suitable conditions were: use of floridin of decreased catalytic activity, low space velocity, and reaction temperature of ~75°. The average molecular weight of the products was 8000. Isobutene was also readily polymerised over a synthetic aluminosilicate catalyst at 40°, to give polymers resembling those obtained with floridin[135]; di-, tri-, and tetramers were obtained.

Slobodin[136] observed that isobutene could be polymerised over a series of bleaching earths. The average molecular weight of the polymer depended on catalyst activity and was less with the more active catalysts. Silica gel did not bring about reaction.

A detailed investigation of isobutene polymerisation over Gayer's synthetic aluminosilicate catalyst was carried out by Kazanskii and Rozengart[137–139]. Polymerisation took place over a wide temperature range, from room temperature to 289°. As the temperature was raised the polymer yield fell; the dimer yield passed through a maximum at ~200° and then fell sharply; the yield of trimer and higher fractions fell sharply. The composition of the polymerised products varied markedly with increase of temperature, and the content of cracking and isomerisation products was raised.

Under the same conditions Butlerov's diisobutene gave a mixture of dimers, trimers, and other isobutene polymers resembling the products obtained by polymerising isobutene over the same catalyst. At 210° depolymerisation of diisobutene to isobutene was also observed. A study of the

effect of adding thorium[137,140] and zirconium[140] to aluminosilicate showed that such triple catalysts are highly active. With them polymerisation took place at 165° and 45 atm. All catalysts were readily regenerated by air at 400°–500°, and the activity of the regenerated catalyst was somewhat higher than that of fresh catalyst. Zinc and thallium have also been mentioned as additives to aluminosilicate catalyst[137]; they deactivate it, as do cobalt and nickel[141-143]. Isobutene has been polymerised over $Al_2O_3-SiO_2-Ni$ at 250°–350° and 4–10 atm[141].

Kazanskii and Rozengart[137] found that the compositions of the products of polymerisation by synthetic aluminosilicate catalyst and "solid" phosphoric acid closely resembled one another. For this reason they ascribed the polymerising capacity of aluminosilicates to their acid properties, and assumed an ionic mechanism for polymerisation of alkenes by such catalysts, a view which was later supported by other workers[144]. The activity of these catalysts, being due to the presence of protons, vanished on neutralisation of the surface acids by absorption of basic compounds[145-148]. It is assumed that the active complex is $(HAlSiO_4)_x$.[147]

Other oxide catalysts. Rapoport et al.[149] carried out one-stage isobutene polymerisation with subsequent dehydrocyclisation of the polymerisation products over $MoO_3-Al_2O_3$ at 300°–450° and atmospheric pressure. In the xylene fraction of the product obtained at 400°, there was 60% of *p*- and *m*-xylenes, a yield of 6 g/m³ of feed gas. At 200° isobutene was polymerised to di- and triisobutenes.

With 1–2% BeO [83,84] isobutene was polymerised at 275°, the yield being 25%. The main product was diisobutene, plus small amounts of triisobutene. Polymerisation took place readily over activated bauxite[150-152] at 120°–175°, both at atmospheric and at higher pressures. Isobutene was not polymerised when passed over Al_2O_3 at 600° [89]. In the presence of Al_2O_3 + HCl [153] isobutene dimerised to give 29.6% of dimer when the initial isobutene concentration was 89.8%. Removal of oxygen from the starting isobutene raised the dimer yield to 45%, while increasing the pressure to 2.5 atm had almost no effect on the dimer yield.

The following conclusions can be drawn from the investigation of the polymerisation of isobutene on oxide catalysts: polymerisation over synthetic and natural aluminosilicates takes place over a wide temperature range, -80° to 290°. Silica gel and Al_2O_3 do not bring about polymerisation, but isobutene is polymerised by Al_2O_3 + HCl.

4. Polymerisation by Alkali Metals

Ostromyslenskii[154] investigated the polymerisation of alkadienes mixed with alkenes by metallic sodium (anionic polymerisation). L'vov showed[155] that when a butadiene–isobutene mixture was polymerised with 2% Na metal, at 20°–25° under nitrogen, the isobutene partly reacted. When the isobutene concentration was increased the relative yield of polymers also rose, and was equivalent to 120 vol.% with respect to butadiene taken when the mixture contained 88% of isobutene. But the product also contained more low polymers (30% in the case mentioned). Among them was a product of addition of isobutene to butadiene, namely 2-methylhepta-1,5-diene, and aliphatic hydrocarbons $C_{12}H_{20}$, $C_{16}H_{28}$, $C_{20}H_{32}$, and $C_{24}H_{38}$, all of which had the general formula $(C_4H_6)_{n-1}C_4H_8$, with *n* double bonds per molecule, (*n* - 1) molecules of butadiene and one molecule of isobutene having reacted.

L'vov considered that polymerisation of butadiene–isobutene mixtures can readily be explained by a chain theory[155]; the formation of low polymers is related to chain termination in the butadiene polymerisation by isobutene reacting with active molecules of growing polymer. A suggested chain termination mechanism[156] is based on the assumption that hydrogen atoms in isobutene can be substituted by metallic sodium, through the agency of active sodio-organic compounds which are formed from Na and the alkadiene:

$$Na(C_4H_6)_nNa + 2\,H_3C(H_3C)C{=}CH_2 \longrightarrow 2CH_2Na{-}C(CH_3){=}CH_2 + H(C_4H_6)_nH \qquad (35)$$

A similar mechanism was observed[157] when isobutene was copolymerised with isoprene under the influence of sodium. With 3% metallic Na, the overall yield of polymer reached 117% with respect to the initial isoprene when the isobutene concentration was raised to 90%, and at the same time the content of low-molecular-weight copolymers increased. Hydrocarbons C_9H_{16} and $C_{14}H_{24}$, products of addition of one molecule of isobutene to one and two molecules of isoprene, were isolated. Copolymerisation of isobutene with ethylene and propene, in the presence of metallic sodium, was observed[158] at 300° and 500–600 atm. A hexene was isolated from the low molecular products derived from isobutene plus ethylene, and a heptene from those derived from isobutene plus propene.

5. Polymerisation by Organometallic Compounds

Ziegler[159] claimed that isobutene was polymerised by $AlCl_2C_2H_5$, though more feebly than by $AlCl_3$, and that it was not polymerised at all (unlike ethylene) by $Al(C_2H_5)_3$ and $Al(C_2H_5)_2Cl$. Topchiev, Krentsel', and coworkers[160] found that polymerisation of isobutene with formation of liquid and rubber-like products took place when $Al(C_2H_5)_3$ + $TiCl_4$ was used. Reaction occurred between -25° and 75° in isooctane, at a molar ratio $AlEt_3 : TiCl_4 = 1 : 2$, the concentration of dissolved $AlEt_3$ being 1 wt.%. The yield of polymers was up to 80% of the initial isobutene and 95% of that reacted. The molecular weight of the polymers increased as the temperature was lowered, from 2000–3000 at +50° to 10 000 at -25°. Reaction time and the $AlEt_3 : TiCl_4$ ratio also affected the molecular weight[161].

6. Hydropolymerisation of Isobutene

Ipat'ev and Komarevsky[162] stated that isobutene and pentene give respectively octane and decane with $Fe-MgCl_2$ catalyst and hydrogen at 250°–300° and 80 atm, and they called the reaction hydropolymerisation. They supposed that the reaction consists of two stages: alkene dimerisation and dimer hydrogenation. NiO can be used instead of Fe, and $ZnCl_2$ or $AlCl_3$ in place of $MgCl_2$. The yield of isobutene polymerisate was 50–90% of the isobutene, depending on the catalyst, and the hydropolymerisate comprised mainly hydrodimer and hydrotrimer.

Eidus and Nefedov[163] found that addition of hydrogen to isobutene substantially affects the course of its polymerisation over a Co-clay catalyst at 190° and atmospheric pressure. Even a small addition of hydrogen, 0.2%, caused considerable increase in polymer yield and in degree of polymerisation. Raising the hydrogen concentration to 50% led to further increase in polymer yield and promotion of the hydrogenation and hydrocracking side reactions. This effect of hydrogen was not observed over a

red clay carrier, though the latter was more active than the Co–clay catalyst, and led to formation of isobutene dimers and trimers. It was shown[164] that the course of hydropolymerisation of isobutene over Co–clay varied with the H_2 content of the feed gas. With no hydrogen, or with a concentration of 0.2–0.3%, the main products were isobutene dimers and trimers, and the reaction mechanism was ionic. At 40–50% hydrogen concentration the main reaction products were 2-methylalkanes and 2-methylalkenes (2-methylbutane, 2-methylpentane, 2-methylhexane, etc., and the corresponding alkenes). In this case reaction evidently involved free radicals formed in the presence of the reduced cobalt.

III. INDUSTRIAL APPLICATION OF PROCESSES FOR POLYMERISING ISOBUTENE

Polymerisation processes involving isobutene are of great practical importance. Thermal polymerisation of alkenes in cracking gases offers a ready method of making liquid motor fuels. The process is operated at 480°–540° and 50 atm, and the resultant gasoline has octane number 75–80.[165]

Sulphuric acid polymerisation of a butene–butane fraction is effected with 60–70% acid either at -20° to +25°, which brings about selective dimerisation of the isobutene, or at 75° to 110°, when the n-butenes also react. The resultant dimer is hydrogenated to isooctane[166–176].

Sulphuric acid is also used to copolymerise isobutene with other alkenes, n-butenes[177], and isopentenes[178,179]. A mixture of octenes and octanes is obtained by polymerising isobutene under the influence of SO_2 at 400° and 182 atm[180]. Anhydrous SO_3 is used as a catalyst for the preparation of low-molecular-weight isobutene polymers[181].

In addition to sulphuric acid, phosphoric acid[182] is used industrially as a catalyst for making high-octane motor fuels and technical isooctane from technical butane–butene mixtures. It is used as the "solid" acid (phosphoric acid on a carrier), in liquid form, or as copper pyrophosphate. Polymerisation of isobutene alone or copolymerisation with other alkenes over a catalyst (e.g. phosphoric acid on a carrier) is usually effected at 50°–200° and 17–63 atm. Carriers for phosphoric acid are: silica gel[183], activated carbon[65], and kieselguhr[184–186]. For example, copolymerisation of isobutene with propene over phosphoric acid[182,187–189] is effected at 135° and 35–42 atm, and copolymerisation with n-butenes at 128°–175°.

Phosphates used as catalysts are[190–194]: phosphates of zinc (solution in H_3PO_4[190,191]), of calcium, copper, cadmium (in H_3PO_4[192]), and cerium[194]. Reaction takes place at 120°–285°, sometimes under pressure (up to 98 atm). For example, with the copper phosphate, selective polymerisation of butene–butane mixtures is carried out at 250° and 60 atm[195,196]. The temperature for non-selective polymerisation is 190°–205°.

It is possible to obtain isomeric octanes by hydropolymerising isobutene at 250°–300° with a hydrogen pressure of 80 atm, using a solid catalyst, phosphoric acid-nickel(II) oxide-iron, when 92–96% of the isobutene reacts, the liquid polymerisate containing 46–56% of octanes, octane number 83–84.[121]

The low-temperature polymerisation of alkenes, and in particular isobutene, in the presence of metal halides, is of great practical importance, because it allows the production of high polymers, which are lubricating oils, lubricating-oil additives, and synthetic rubbers and plastics[79].

Low-temperature polymerisation is usually effected in the liquid phase with a diluent and 0.1% (with respect to the isobutene starting material) of catalyst. Isobutene is polymerised alone or copolymerised with alkenes[123,125,197–202], conjugated alkadienes[126,200,203–222], cycloalkenes[223–227], and alkyl acetylenes[209]. Suitable diluents are: alkyl halides[125,226–231], carbon tetrachloride[199,232], aliphatic esters[233,234], ketones[123,235,236], ethers[226*], nitrous esters[236,237,238], hydrocarbons[123,125,198,199,236–241], alcohols[213,242,243], carbon disulphide[231,244], and carbon dioxide[209]. The following can be used to accelerate reaction: sulphuric acid, nitric and trichloroacetic acids, formaldehyde, phenol, cresol, aliphatic, cycloalkyl, and aromatic alcohols[126], carbon dioxide, ethers[234], and hydrogen halides[245]. Sometimes up to 1% of a catalyst poison (S, H_2S, or organic sulphur compounds) is added[241,246]. Addition of hydrogen halides, anhydrous HF or HCl can lower the molecular weight of the polymer, although at room temperature such compounds facilitate polymerisation of alkenes by metal halides, which is often carried out in emulsions.

Emulsion polymerisation has a number of advantages: possibility of better control of the process, prevention of overheating, preparation of homogeneous hydrocarbons, etc. It can be applied only in a limited temperature range, which can, however, be extended by employing media of fluorohydrocarbons, e.g. perfluoro-*m*-xylene, and a mixture (1:3) of perfluoromethylnaphthalene and perfluoromethylcyclohexane[247]. Both of these solvents remain liquid between -95° and 80° and do not mix with the isobutene or butadiene at temperatures below the boiling points of these hydrocarbons; in addition, polymerisation catalysts ($AlCl_3$, BF_3) have practically no action on them at room temperature or below. Polymerisation takes place readily at -70° in a well-mixed emulsion system when the catalyst is introduced in a finely-divided state or dissolved in the perfluorohydrocarbon or in ethyl chloride. Isobutene is usually copolymerised with butadiene. The molecular weight of the polymerisation products falls considerably as the butadiene content of the starting mixture is increased. Low-molecular-weight copolymers are obtained when isobutene is copolymerised with isoprene or 2,3-dimethylbuta-1,3-diene.

An example of the industrial use of low-temperature polymerisation is the process for making Oppanol. This is carried out with BF_3 at -80° to -90° using a diluent (usually isobutane). Depending on the solvent : isobutene ratio, either a lubricating oil or a solid plastic material (Oppanol, Vistanex) is obtained. Various aspects of the process are discussed in the patent literature[106–109,197,198,232–234,248–268]. There is also an industrial process for polymerising isobutene plus 2% alkadiene, using $AlCl_3$ as a catalyst, to give a synthetic rubber (butyl rubber)[269–273]. The process is carried out at -90° to -100° using a diluent (methyl chloride). The catalyst for polymerisation and copolymerisation with other unsaturated compounds may be $AlCl_3$[90,123,125,126,197–208,221–230,235,242,261–263,274–285] as well as $AlBr_3$[125,126,209,229,281], $AlBrCl_2$, $AlBr_2Cl$, and the complexes $Al(OC_2H_5)_3 \cdot 3AlCl_3$[215]; $AlOBr \cdot 4AlBr_3$[200,209,229,276]; $AlBr_2I \cdot AlOI$, $AlBr_3 \cdot AlOBr$, $4AlBr_3 \cdot AlOBr$, $6AlBr_3 \cdot AlOBr$, $4AlBr_3 \cdot TiOCl_2$[200,286]; $AlCl_2OH$[229,230], $AlBr_2OH$, $AlBr_2Cl \cdot AlOCl$[229], $AlBrCl_2 \cdot AlOBr$, $AlBr_3 \cdot Br_2CS_2$[278], Al_2ClBr_5[240], $AlCl_3 \cdot CH_3OCH_3$[235,236], $AlCl_3 \cdot C_2H_5COCH_3$[235], $AlBrCl_2 \cdot AlOBr$, $AlCl_3 \cdot Al(OC_2H_5)_3$, $AlBr_3 \cdot AlBr_2OH$[229], and $TiCl_4$[98,125,126,197,229,237,254,276] and its complexes:

* Ethers are not mentioned in ref. 2 26 (Ed. of Translation).

$TiCl_2(COCH_3)_2$, $TiCl_3(COCH_3)$ [287], $TiCl_4 . AlCl_2OH$, $TiOCl_2 . TiCl_4$ [229], and $SnCl_4$ [123,126].

The information given above shows that polymerisation and copolymerisation of isobutene are widely used industrially. Of special importance are processes for polymerising isobutene and butane–butene mixtures to yield technical isooctene (subsequently hydrogenated to isooctane), using sulphuric and phosphoric acids, and low-temperature polymerisation processes involving isobutene with a Gustavson–Friedel–Crafts type of catalyst (BF_3, $AlCl_3$) for making high quality lubricating oils, synthetic rubbers, and plastics.

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MACROMOLECULAR DIELECTRICS

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INTRODUCTION

If a polymer is to be used as an electrical insulator or a dielectric, not only its electrical properties but also a number of other physicochemical properties must fulfil certain conditions. The fact that a given polymer has certain electrical properties is no guarantee that it will be of any practical use. For example, some polymers are ruled out because their thermal stability is poor, because they are difficult to work, or because their mechanical strength is low.

Our aim in this paper is to demonstrate certain regularities in the electrical properties of polymers, using data from our own publications and from those of other investigators. Attention will mainly be directed to dielectric loss and polarisation, and their relation to the structure of the polymers. In this connection we shall not only consider the chemical composition, stereochemical structure, and crystalline or amorphous state, but also the nature of the thermal motion, since the latter has a marked effect on the electrical properties. The main peculiarity of the thermal motion of a polymer macromolecule is that, because of its chain-like structure and relatively enormous dimensions, intramolecular thermal motions play an important part.

Polymers may be divided into polar and non-polar, according to the stereochemical structure of the monomers; the overwhelming majority are polar. The variation of the electrical properties of polar polymers may be explained in terms of the nature and strength of the molecular forces. Study of the effective dipole moment of these polymers has shown that intramolecular forces are predominant[1], while in substances of lower molecular weight the intermolecular forces are most important.

A number of the electrical properties of polymers are kinetic in nature, so the study of these substances in changing electrical fields is of great interest. This is also worth while from the practical point of view, because dielectrics are used more often in alternating than in constant electric fields.

1. DIELECTRIC LOSSES AND POLARISATION OF NON-POLAR POLYMERS

Non-polar polymers are extensively used as high-frequency dielectrics. The most important electrical properties of such substances are the tangent of the dielectric loss angle, $\tan\delta$, and the dielectric constant ϵ'.

We shall first consider the dependence of these quantities on frequency and temperature for the most widely investigated polymer, amorphous polystyrene (PS).

Fig. 1 shows $\tan\delta$, ϵ', and n_D^2 (the square of the refractive index) for PS as functions of temperature at a frequency of 10 kc/s,[2] and $\tan\delta$ and ϵ' as functions of frequency at two temperatures, one below and one above the vitrification temperature, $T_{vtr} = 80°$. It may be seen from Fig. 1*b* that $\tan\delta$ and ϵ' are practically independent of the frequency for vitreous PS (i.e. for $T < T_{vtr}$). The value of $\tan\delta$ is $(0.5-1)\times 10^{-4}$, and this does not vary much with the temperature for $T < T_{vtr}$. The decrease of ϵ' on heating in this temperature range is connected with the thermal expansion of the sample. Thus, it may be seen from Fig. 1 that there is a break in the ϵ' vs. T curve at about the vitrification temperature, which is also found in the density vs. temperature curve. The values of ϵ' and n_D^2 for PS coincide within 1% over a wide range of temperatures.

All this shows that relaxation-dependent dipolar dielectric losses do not occur in vitreous PS. It may also be seen from Fig. 1 that at temperatures above T_{vtr}, the $\tan\delta$ vs. T and $\tan\delta$ vs. $\log f$ curves both show maxima. Near these maxima the value of ϵ' begins to decrease with the frequency and increase with the temperature. These are signs of dipolar polarisation. The presence of dipoles in PS may be due either to impurities chemically bound to the chain or to the slight polarity of the monomer ($\mu \sim 0.1-0.3$ c.g.s. units).

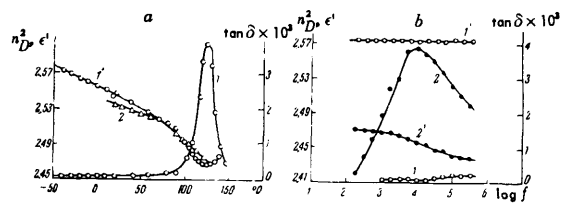


Fig. 1. The dielectric constant, square of the refractive index, and tangent of the dielectric loss angle of polystyrene as functions of temperature (*a*) and frequency (*b*)[2]. *a*: 1), 1') $\tan\delta$ and ϵ' at 10^3 c/s; 2) n_D^2. *b*: 1), 1') $\tan\delta$ and ϵ' at 39°; 2), 2') $\tan\delta$ and ϵ' at 134.5°.

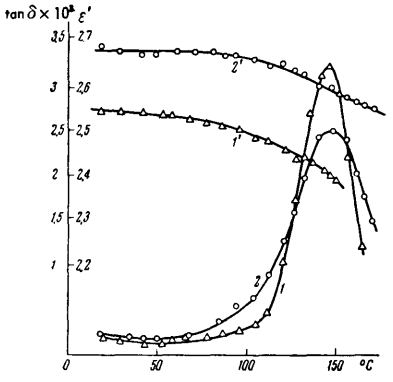


Fig. 2. ϵ' and tan δ for polystyrene as functions of temperature at 8.5×10^4 c/s: 1), 1') tan δ and ϵ' of atactic polystyrene; 2), 2') tan δ and ϵ' of isotactic polystyrene[3].

Fig. 2 shows ϵ' and tan δ as functions of the temperature for atactic and isotactic polystyrene[3]. It will be seen that both the values of these quantities and the way in which they vary with temperature are very similar for these two types of polystyrene. The slightly higher values of ϵ' for isotactic PS is due to the greater density of this substance. The temperature at which tan δ is maximum is the same for the two forms of PS, which is in accordance with the equality of the vitrification temperatures for these polymers[4]. Near the maximum the value of tan δ is nearly the same for both polymers. The slightly higher value for atactic PS may be due to the presence of traces of catalyst, which increases the value of tan δ as will be shown below for the case of polyethene (PE).

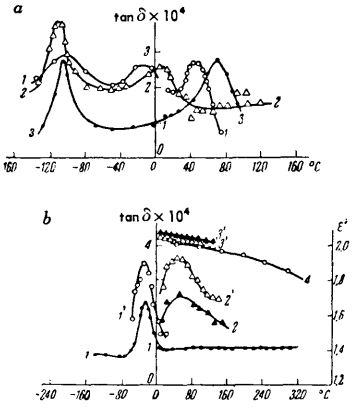


Fig. 3. ϵ' and tan δ for polyethylene (*a*) and F-4 (*b*) as functions of temperature[5,6,7]. *a*: 1), 3) high-pressure and low-pressure polyethylene; 2) "quenched" PE_{LP}. *b*: 1), 1'), 2), 2') tan δ of original and "quenched" samples at 10^3 and 5×10^8 c/s; 3), 3') ϵ' of original and "quenched" samples at 5×10^8 c/s; 4) ϵ' at 10^2 and 10^5 c/s.[4]

It may be expected that the dielectric properties of crystalline polymers will depend on the crystalline state of these substances: in fact, we have already seen how an increase in density on crystallisation of polystyrene is accompanied by a slight (about 1.5%) increase in the dielectric constant.

Fig. 3 shows tan δ as a function of temperature for low-pressure polyethylene, high-pressure polyethylene and polytetrafluoroethylene (PE_{LP}, PE_{HP}, and F-4)[5,6,7]. Some of these curves (curves *1'* and *2'* in Fig. 3*b* and curve *2* in Fig. 3*a*) refer to samples of low crystallinity, produced by rapid cooling from the liquid state. All the curves in Fig. 3 were determined at temperatures above T_{vit}: the vitrification temperature for F-4 is about -100°, and experiments on the dynamic mechanical losses of PE indicate that its vitrification temperature is about -140°.[8]

It will be seen that above the vitrification temperature the tan δ vs. T curve for F-4 has one maximum, and the corresponding curves for PE_{LP} and PE_{HP} have two and three maxima respectively. Since we are dealing with crystalline polymers, these dipolar losses may be associated with dipolar relaxation in the amorphous or in the crystalline part. It was found that the value of tan δ for F-4 in the region of the maximum is increased if the degree of crystallinity is reduced by rapid cooling from the liquid state, which suggests that these losses are connected with processes in the amorphous part of the polymer.

The picture is rather more complicated for polyethylene. The increase in the branching of the molecule on passing from PE_{LP} to PE_{HP} leads to a considerable change in the nature of the relation between tan δ and the temperature: at a frequency of 1 kc/s near 0° the more highly branched PE_{HP} shows a maximum due to the "medium-frequency relaxation losses" (m.f.r. losses), which is not found with PE_{LP}.

We have seen that ϵ' for polystyrene is constant to within 1% with respect to frequency, and that the decrease of ϵ'

TABLE 1.

Polymer	t, °C	ϵ'	d, g/cm³	P, cm³, obs.	R_D, cm³, calc.	$\frac{(P-R_D)}{P} \times 100$, %
Atactic polystyrene	25	2.544	1.055	34.3	33.7	1.8
Isotactic polystyrene	25	2.680	1.075	35.0	33.7	4.0
Polyethylene	23	2.276	0.920	4.55	4.65	2.2
Polyethylene	23	2.320	0.940	4.56	4.65	2.0
Polyethylene	23	2.365	0.960	4.56	4.65	2.0
Isotactic polypropylene	25	2.28	0.912	13.6	13.9	2.2
Atactic polypropylene	25	2.16	0.865	13.6	13.9	2.2

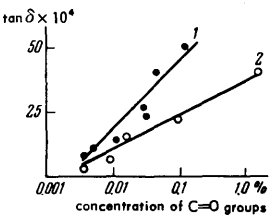


Fig. 4. The variation of tan δ for polyethylene with the concentration of C=O groups: 1) PE_{HP}, 25°C, 5×10^7 c/s[14]; 2) PE_{LP}, 20°C, 400 c/s[15].

with temperature is due to thermal expansion. Similar results are obtained for other non-polar polymers. For such polymers ϵ' lies between 2.0 and 2.6 (F-4 and PS), and is determined by the values of the density and the bond refraction. The accuracy of this relationship is shown in Table 1, in which are given measured values of ϵ' and the density for various polymers at various temperatures, the values of the molecular polarisation calculated from these data, and the molecular polarisation determined from bond-refraction data given in the literature[9]. The last column gives the percentage difference between the experimental[7,10,11] and calculated values. It will be seen that this difference never exceeds 4%. It may therefore be concluded that the value of ϵ' for non-polar polymers is practically entirely determined by deformation polarisation. Changes in the density can only have a slight effect on ϵ'. For example, PE_{HP} has $d = 0.92$ g/cm³ and $\epsilon' = 2.28$, while PE_{LP}, with $d = 0.96$ g/cm³ has $\epsilon' = 2.36$ to 2.37. The value of ϵ' for polystyrene or polyethylene foams may be 1.1–1.2. Investigation of the possibility of using such materials in cables is therefore of great interest.

A substance with a high dipolar or ionic polarisability is sometimes added to a non-polar polymer in order to increase ϵ'. However, this is always accompanied by an increase of $\tan\delta$ for certain temperatures and frequencies. This way of increasing ϵ' is only acceptable for capacitors to be used in relatively narrow ranges of frequency and temperature. For example, in the USA[12] F-4 containing 20% of barium titanate has been used for high-frequency capacitors. This material has $\epsilon' = 5$, and $\tan\delta$ of the order of 0.001.

The value of $\tan\delta$ near the maximum is proportional to the volume fraction of polar groups present, and to the square of their effective dipole moment μ_{eff}.[13] The presence of these groups in non-polar polymers may be due to either a disturbance in the structure of the macromolecular chain (oxidation, appearance of unsaturation) or impurities. Fig. 4 shows $\tan\delta$ for high-pressure and low-pressure polyethylene, as a function of the concentration of the highly polar C=O groups in the polymer molecule, determined from the infra-red absorption spectra[14,15]. It may be seen that concentrations of the order of 0.005% correspond to $\tan\delta = 0.0005$. This amount of C=O groups is so small that it can hardly be determined spectroscopically; but the value of $\tan\delta$ for these polymers is quite high, so that they cannot be used for some ultra-high-frequency applications. The oxidation of polypropylene (PP) also strongly increases the value of $\tan\delta$. It will be seen from Fig. 5 that rolling

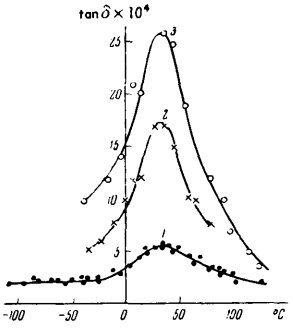


Fig. 5. $\tan\delta$ for polypropylene as a function of temperature at 7.5×10^4 c/s: 1) original sample; 2) after rolling for 10 min at 170°; 3) after rolling for 20 min at 170°.

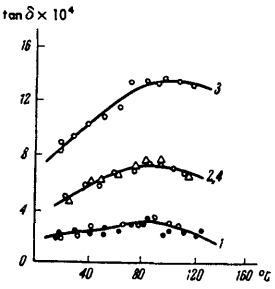


Fig. 6. $\tan\delta$ for polyethylene as a function of temperature at 3×10^9 c/s[16]: 1) PE_{LP}, ash content S = 0.03%; 2) PE_{LP}, S = 0.35%; 3) PE_{LP}, S = 1.9%; 4) PE_{HP}.

molten PP for only 10 min increases $\tan\delta$ more than three times, from $(2-5) \times 10^{-4}$ to $(6-17) \times 10^{-4}$. The data given above suggest that these losses are due to the presence of small amounts (0.01–0.001%) of polar groups (OH, C=O, etc.).

Organometallic catalysts are now very widely used. Polymers made with the aid of these catalysts should be very carefully purified.

Fig. 6 shows $\tan\delta$ as a function of the temperature at 3×10^9 c/s for samples of PE_{LP} which have been purified with varying thoroughness[16], as determined by the amount of inorganic material in the polymer. It may be seen from Fig. 6 that the removal of traces of catalyst has a considerable influence on the value of $\tan\delta$. Thus, at 80° and $f = 3 \times 10^9$ c/s, polyethylene with an ash content of 0.03% has $\tan\delta = 3 \times 10^{-4}$, while an ash content of 1.9% gives $\tan\delta = 13.5 \times 10^{-4}$. All this shows that in order to obtain non-polar polymer dielectrics with the lowest possible value of $\tan\delta$ (about 0.0001) over a wide range of frequency and temperature, extreme care must be taken in the production and processing to ensure the absence of impurities and of polar groups in the macromolecule.

Moreover, in a number of cases differences in the structure of the macromolecule can have a considerable effect on the value of $\tan\delta$. Thus, it has been mentioned above that PE_{HP} shows three sorts of dipolar losses, while PE_{LP} shows two. It is known that at room temperature and above PE_{HP} and PE_{LP} have a maximum in the dielectric losses at ultra-high frequencies[17], and that in the region of this maximum PE_{HP} shows two kinds of losses simultaneously, while PE_{LP} only shows one: it lacks the medium-frequency relaxation. This is why the value of $\tan\delta$ for PE_{HP} is about twice that for PE_{LP} at ultra-high frequencies, other things being equal (purity, moisture content, etc.) (see Fig. 6, curves *1* and *4*).

2. DIELECTRIC LOSSES AND DIELECTRIC CONSTANTS OF POLAR POLYMERS

Fig. 7 shows $\tan\delta$ and ϵ' as functions of temperature for poly-*p*-chlorostyrene (PPCS),[18] polyvinyl chloride (PVC)[19] and polytrifluorochloroethylene (F-3).[20] These substances differ from PS, PE, and F-4 respectively in that one atom of hydrogen or fluorine is replaced by chlorine in the monomer. This is accompanied by a considerable increase in

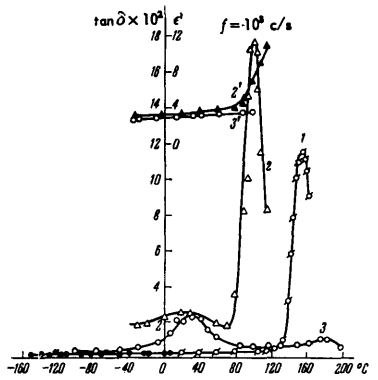


Fig. 7. ϵ' and tan δ for polar polymers as functions of temperature at 10^3 c/s: 1) tan δ for polyparachlorostyrene [section marked —·—· at 10^6 c/s (missing from figure. Ed. of Translation)] [18]; 2), 2') tan δ and ϵ' for polyvinylchloride [19]; 3), 3') tan δ and ϵ' for F-3 [20].

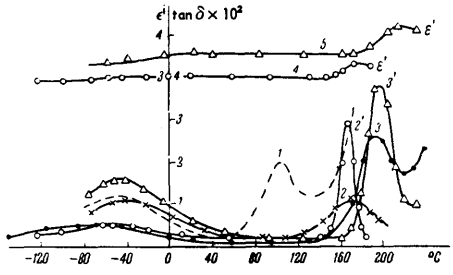


Fig. 8. ϵ' and tan δ for polyesters as functions of temperature at 10^3 c/s [23, 24]: 1) tan δ for polyethyleneterephthalate[23]; 2), 2') tan δ for poly-dian-carbonate (curve 2' — sample of reduced crystallinity); 3), 3') tan δ for poly-dian-isophthalate; 4), 5) ϵ' for poly-dian-carbonate and poly-dian-isophthalate.

the dipole moment μ_{eff}; in fact, all the physical and mechanical properties are changed. It may be seen from Fig. 7 that the maximum value of tan δ is 0.1–0.2, and $\epsilon' = 4$–10 for these polar polymers. This is doubtless due to the polarity of the monomer: the relationship between ϵ' and tan δ of polymers on the one hand and μ_{eff} and the concentration of dipoles n_0 on the other has received ample experimental confirmation.

Moreover, measurement of the dielectric losses has been successfully used in a number of cases to determine the value of the dipole moment or the concentration of dipoles [17]. As may be seen from Fig. 7, the maximum value of tan δ for polar polymers is 100 to 10 000 times larger than for non-polar polymers. This makes it difficult to use polar polymers as high-frequency dielectrics. It is interesting that at temperatures below T_{vit} the value of tan δ for PPCS hardly changes with temperature, and does not exceed 0.001. Similar data have been obtained with three other polymers of halogenated styrene [18]. This property of a given set of polar polymers is evidently connected with the specific properties of the polar side group.

It may also be seen from Fig. 7 that the curves of tan δ as a function of temperature for PVC and F-3 both have two maxima. The dipole losses occurring at low temperatures are called dipolar-radical (d.r.) losses, while those occurring where the polymer is highly elastic are called dipolar-elastic (d.e.) [3] losses. These two types of losses have been discovered in the vast majority of polymers investigated, both amorphous and crystalline [13,22]. Even when measurements of tan δ and ϵ' seem to indicate that d.r. losses are absent [18], more detailed analysis of the frequency-dependence of tan δ and ϵ' shows that both d.r. and d.e. losses are present, but cannot be distinguished at frequencies between 50 and 10^{10} c/s.

Fig. 8 shows tan δ and ϵ' as functions of temperature for three crystalline polyesters: polyethyleneterephthalate (PET), [23] poly-dian-carbonate* (PDC) and poly-dian-isophthalate* (PDIP), [24] and for the less crystalline samples of the last two (curves 2' and 3').

It may be seen that, despite the differences in structure, the dipolar loss for all these polymers in the low temperature range has its maximum at the same temperature. Remembering that these polyesters contain highly polar carbonyl groups, the explanation of the constant value of T_{max} may be that the other atoms and groups play no essential part in the dipolar-radical relaxation process.

A different rule holds for the dipolar-elastic losses, occurring at higher temperatures: the temperature at which tan δ is a maximum increases with the number of aromatic groups in the macromolecule.

As may be seen from Fig. 8, crystallisation of the polymers is accompanied by a decrease in the value of tan δ. This has been observed in other crystalline polymers [25].

In Table 2 are given data on the effect of crystallisation of polychloroprene (PCP), PET, and F-3 on the value of the loss factor $\epsilon'' = \epsilon' \tan\delta$ in the region of maximum d.e. and d.r. losses, and also values of α, the characteristic width of the relaxation-time spectrum or the range of frequencies corresponding to the region of maximum dielectric loss. At the maximum the loss factor ϵ''_m is related to α, n_0, and μ_{eff} as follows:

$$\epsilon''_m = \epsilon' \tan\delta = A \frac{\alpha n_0}{T} \mu^2_{eff}. \qquad (1)$$

It may be seen from Table 2 that crystallisation decreases the value of ϵ'', and the value of α for d.e. losses, while the value of α for d.r. losses remains practically unchanged. This suggests that d.e. and d.r. losses in crystalline polymers are connected with relaxation processes in amorphous regions of the polymer. The decrease of ϵ' and tan δ on crystallisation may be related to a decrease of the concentration of dipoles in these regions. However, in the case of the d.e. losses this decrease in ϵ''_m is partly due to a decrease in the value of α as a result of the increase in the heterogeneity of the structure of the polymer on crystallisation. We may remark that orientation of the dipoles may occur in the well-ordered crystalline regions of polymers, leading to a sharp increase of ϵ' on crystallisation, as has been observed in certain substances of low molecular

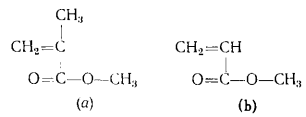
* "dian" = "Bisphenol A" = di(P-hydroxyphenyl)dimethyl methane (Ed. of Translation).

TABLE 2. The effect of the degree of crystallinity X on the loss factor ϵ''_m and the parameter α governing the distribution of relaxation times[25].

Polymer	f, c/s	Sample 1, with lower degree of crystallinity			Sample 2, with higher degree of crystallinity			Remarks
		X_1	$\epsilon''_{m_1}=\epsilon'_{m_1}\tan\delta_1$	α_1	X_2	$\epsilon''_{m_2}=\epsilon'_{m_2}\tan\delta_2$	α_2	
Polychloroprene	10^4	0	1.0	0.48	0.04	0.75	0.43	dipolar-elostic losses
		0	1.0	0.48	0.19	0.66	0.36	
		0	1.0	0.48	0.36	0.58	0.32	
PET	$5\cdot10^2$	0	0.49	0.48	0.60	0.12	0.24	ditto
	$2\cdot10^2$	0	0.45	0.44	0.60	0.11	0.22	
	$6\cdot10^4$	0	0.067	0.30	0.60	0.041	0.31	dipolar-radical losses
	$9\cdot10^5$	0	0.055	0.31	0.60	0.039	0.31	
F-3	50	0.3	0.070	0.20	0.55	0.054	0.26	ditto
	$2\cdot10^4$	0.3	0.12	0.50	0.55	0.078	0.50	
	$4.5\cdot10^5$	0.3	0.13	0.60	0.55	0.082	0.60	

weight[26]. This also occurs to a certain extent in F-3, for which the value of ϵ' decreases by about 20–30% on fusion[20].

A convenient method of controlling the physicochemical properties of polymers is copolymerisation. Fig. 9 shows $\tan\delta$ as a function of temperature for copolymers of styrene with methyl methacrylate (a) and methyl acrylate (b)[13,27].



Methyl methacrylate (MMA) differs from methyl acrylate (MA) in that the α hydrogen in the latter is replaced by a methyl group. This structural difference has a considerable effect on the properties of the polymers and copolymers of these substances. Thus, T_{vit} for PMMA is 110°–120°, while for PMA it is about 25°. It may be seen from Fig. 9 that increasing the concentration of styrene shifts the regions of maximum d.r. and d.e. losses to lower temperatures for copolymers of styrene and MMA. This shift is not found for d.r. losses in copolymers with MA, while the d.e. losses shift to higher temperatures.

It follows from Fig. 9 that the magnitude of the d.e. and d.r. losses of copolymers of polar and non-polar monomers decreases as the concentration of the polar component decreases. It may be remarked that in some cases the opposite behaviour is observed. For example, it may also be seen from Fig. 9 that on going from pure PMMA to the copolymer containing 40% of styrene, the maximum value of $\tan\delta$ in the d.e. loss region increases. This is probably due to an increase in the mobility of the chain as the concentration of α methyl groups is decreased.

In some of the copolymers the presence of d.e. and d.r. losses is indicated in the plots of $\tan\delta$ against frequency, as well as in the temperature curves. Thus, for the copolymer of styrene and MMA , the maximum of $\tan\delta$ at low frequencies (Fig. 10) is due to d.e. losses and the maximum at high frequencies is due to d.r. losses. This example shows that in highly elastic states d.r. and d.e. relaxation may both be found at the same temperature.

The strong influence of the chain structure on its mobility is demonstrated by the example of copolymers of acrylonitrile with butadiene (SKN-26) and styrene (SN-28).[28] Both copolymers contain 26–28% of the polar acrylonitrile.

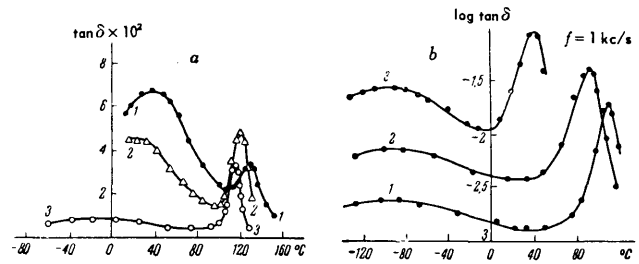


Fig. 9. $\tan\delta$ for copolymers of styrene with methyl methacrylate (a) and with methyl acrylate (b) as a function of temperature. a: 20 c/s, 1), 2), 3) MMA content 100, 80.5, and 24.4%; b: 10^3 c/s; 1), 2), 3) MA content 14, 40, and 100%.

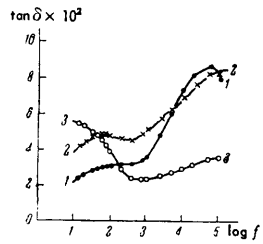


Fig. 10. $\tan\delta$ as a function of the frequency for copolymers of styrene and MMA: 1) 80.2% MMA; 125°; 2) 80.5% MMA, 122.5°; 3) 55.5% MMA, 109°.

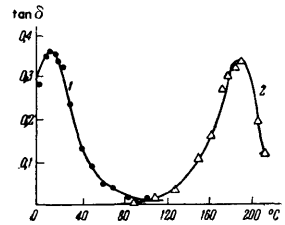


Fig. 11. $\tan\delta$ as a function of the temperature at 1.5×10^6 c/s for copolymers of: 1) acrylonitrile and butadiene, 26 : 74; 2) acrylonitrile and styrene, 28 : 72.

It may be seen from Fig. 11 that the d.e. losses for SKN-26 are maximum at 15°, while the corresponding maximum for SN-28 occurs at 185°. Moreover, the maximum value of $\tan\delta$ is about the same for both copolymers, because they both contain about the same number of $-C\equiv N$ groups. The difference in the temperature of the maximum shows that the d.e. losses are due not only to the thermal motion of the individual polar groups, but also to the thermal motion of segments of the macromolecule.

In non-polar polymers ϵ' decreases with increasing temperature, but in polar polymers it increases with temperature in the regions of d.r. and d.e. losses. Fig. 12 shows

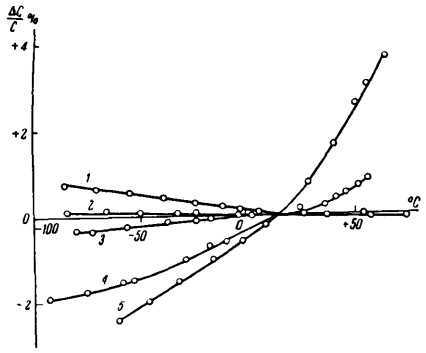


Fig. 12. The relative change of capacitance of capacitors made from copolymers of styrene and MMA, as a function of the temperature at 50 c/s: 1), 2), 3), 4), 5) 0.5, 10, 40, and 60% MMA [26] [one percentage missing (Ed. of Translation)].

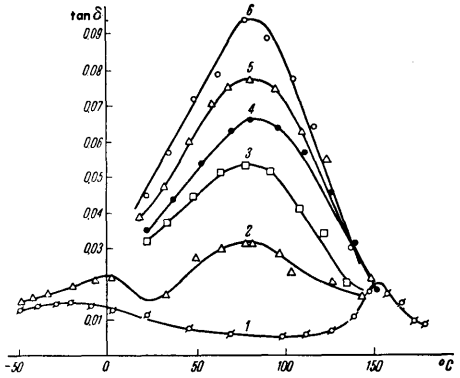


Fig. 14. tan δ as a function of temperature at 10^3 c/s for mixtures of grafted and homopolymers of cellulose acetobutyrate and PMMA: 1), 2), 3), 4), 5), 6) 0, 25, 60, 80, 90 and 100% MMA [28].

how the capacitance of capacitors made with copolymers of styrene with varying amounts of MMA, is related to temperature [26]. It will be seen that a change of temperature from -80° to +60° causes an increase of 6% in the capacitance when a copolymer containing 60% MMA is used, while for a copolymer containing 5% MMA the capacitance decreases by about 0.2%. These data show that copolymers of non-polar monomers with a small amount of polar ones may be used as materials for capacitors with a low temperature coefficient of capacitance.

Polymer dielectrics are quite often plasticised in order to improve their operational characteristics. Fig. 13 shows tan δ and ε' as functions of temperature for polystyrene plasticised with 6.4% of benzyl benzoate [2]. Comparison of these data with those for pure PS (Fig. 1) shows that the introduction of a polar plasticiser increases the value of tan δ about tenfold at temperatures below T_{vit}, and increases the value of ε' by about 10% in this temperature range. This is due to the fact that at low temperatures the values of tan δ and ε' for the PS–benzyl benzoate system are determined to a large extent by the dipolar losses of the second component, i.e. the system is heterogeneous in the vitreous state, and each component has the losses it would have in the pure state. Thus, it has been established that the introduction of a plasticiser has no effect on the temperature or frequency at which d.r. losses are maximum [13,29]. In the highly elastic state plasticising causes a considerable shift of the region of maximum d.e. losses to lower temperatures or higher frequencies, which gives the same results as a decrease in the vitrification temperature.

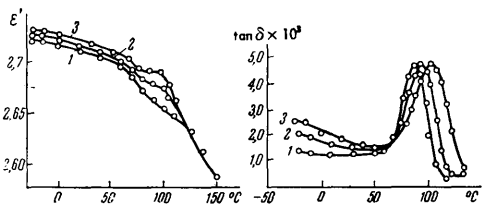


Fig. 13. ε' and tan δ as functions of temperature for polystyrene containing 6.4% benzyl benzoate [2]. 1), 2), 3) 178, 10^3, and 10^4 c/s.

Nowadays the mechanical properties are sometimes improved by grafting a polymer of different chain structure on to the macromolecule, or by making a block-polymer The isolation of the pure graft- or block-polymers from their mixtures with the original substances is sometimes complicated, but fortunately it is not necessary, since the mechanical properties are also improved without it.

The dielectric losses of such technical mixtures of graft- or block-polymers with the homopolymers have been investigated [28]. Fig. 14 shows tan δ as a function of T for poly-(methyl methacrylate), cellulose acetobutyrate (CAB) and mixtures of these substances, containing 25, 60, 80, and 90% MMA. In this case the "grafting" is accomplished by the polymerisation of MMA on the active centres produced in the CAB chain by ultra-violet light. It may be seen from Fig. 14 that at 1 kc/s and 80° PMMA shows a maximum in tan δ. The maximum value of tan δ decreases linearly as the concentration of CAB is increased. Similar data have been found for other polymers which have been modified either during the polymerisation or by a mechano-chemical treatment.

All these data suggest that the values of tan δ and ε' are mainly determined by the concentration of the components. Moreover, each component retains a practically constant relaxation time, which determines the position of the corresponding maximum of tan δ; as is also found with simple mechanical mixtures. Thus, the chemical bonds between the components of a block-polymer, which have a considerable effect on some mechanical properties, have practically no influence on the relationship between tan δ and the temperature and frequency for the separate components.

The orientation of polymeric films and threads gives a considerable improvement in the mechanical properties, and is used for this purpose, for example, in the construc-

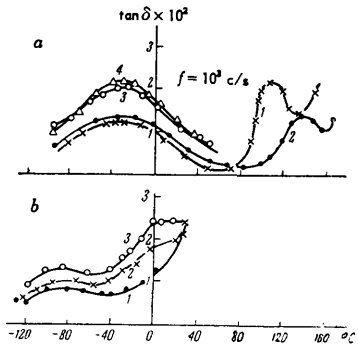


Fig. 15. tan δ as a function of temperature at 10^3 c/s for polyethylene terephthalate (*a*) and nylon (*b*)[30]. *a*: 1), 2), 3), 4) unoriented sample, and samples oriented at 120°, 60°, and 20°. *b*: 1), 2), 3) unoriented sample, and samples oriented in one and two directions.

tion of capacitors. Fig. 15 shows tan δ as a function of temperature for unoriented and oriented films of PET and poly-(hexamethylene adipamide) (nylon)[30]. It will be seen that orientation causes an increase in tan δ in the region of d.r. losses. Moreover, orientation at low temperatures, and in two mutually perpendicular directions, gives a greater increase in tan δ than uniaxial elongation at temperatures above T_{vit}. It may be seen from Fig. 15 that the values of tan δ for oriented PET are lower than for unoriented in the region of d.e. losses, and shifted towards higher temperatures. Similar results have also been found for various amorphous polymers[31].

Finally, Fig. 16 shows the logarithms of the frequencies of maximum d.e. and d.r. losses of certain polymers, plotted against the reciprocal of the absolute temperature[13]. These curves give an idea of the regions of temperature and frequency in which d.r. and d.e. losses are found, and give some information about the mechanism of these losses. D.r. losses are found in the temperature range in which the polymers are vitreous; in this state the polymers have a

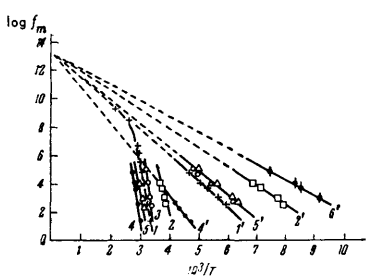


Fig. 16. The logarithm of the frequency of the maximum in tan δ for dipolar-elastic and dipolar-radical losses, as a function of $1/T$ (curve numbers with primes refer to d.r. losses): 1) polymethylacrylate; 2) polypropylacrylate; 3) polychloroethylacrylate; 4) polyvinylacetate; 5) poly-β-chlorovinylpropionate; 6) polyvinylbutyral.

large relaxation time, which is not affected by crystallisation, orientation, copolymerisation, or plasticising. Extrapolation of the curve of $\log f_m = \varphi(1/T)$ for the d.r. losses to $1/T = 0$ gives a frequency of 10^{13}–10^{14} c/s, which is characteristic of processes not related to changes in the short-range order. The activation energy of the d.r. losses can be calculated from the slope of these curves. It lies in the range 5–12 kcal/mole.

All this suggests that the d.r. losses are due to the orientation of small parts of the macromolecule such as separate side groups or a single unit of the chain. The latter probably occurs when a polar radical is firmly bound to the chain (PVC, F-3). In such polymers the relaxation time for d.r. losses is slightly changed by crystallisation or plasticising[13].

D.e. losses occur when the polymer is highly elastic, and the macromolecular chain is very mobile. The relationship between $\log f_m$ and $1/T$ is not linear over a wide range of temperatures (see curve *1* for PMA in Fig. 16). Similar results have been found for other polymers[13]; it is therefore impossible to determine the activation energy of the d.e. losses from the slope of these curves. Earlier, Kobeko[26] had shown that this is characteristic of processes connected with a reorganisation of the short-range order. Thus we may suppose that d.e. losses are due to the thermal motion of relatively large segments of the chain.

Sometimes d.r. and d.e. losses overlap very closely. A typical example is PMMA, for which it is only possible to distinguish the two types of losses in the temperature-dependence of tan δ at very low frequencies, 10–20 c/s. On the other hand, PMA only shows this overlapping at high temperatures and ultra-high frequencies. As Fig. 16 shows, the experimental points corresponding to the maximum of tan δ at frequencies of 10^8–10^9 c/s might refer to the curve for d.e. losses or to that for d.r. losses.

3. ELECTRICAL CONDUCTIVITY AND BREAKDOWN OF POLYMERS

While hundreds of papers have been written on the dielectric losses and polarisation of polymers, comparatively little work has been done recently on their electrical conductivity and breakdown.

The study of the electrical conductivity of polymers is complicated by the fact that the current flowing through a sample under the influence of a constant voltage decreases with time. For example, Fig. 17 shows the logarithm of the current flowing through samples of PE, PS, F-3, F-4, and PMMA as a function of the logarithm of the time for which the constant voltage has been applied[32]. It will be seen that the relationship is a linear one. The value of the current decreases about a thousand times between t = 10 sec and t = 1000 sec for PMMA, F-4 and F-3, so the value of the resistance determined by the usual equation $R_t = V_t/I_t$ is a function of the time.

Fig. 18 shows the volume resistivity of PVC plasticised with 4.5% dioctyl phthalate as a function of temperature, after the voltage has been applied for various periods of time. It will be seen that at temperatures up to about 80° the value of ρ_v increases considerably if the voltage is applied for longer periods, but that this is not the case at higher temperatures[33].

It has been shown by Ioffe[34] that this is due to the production of a large counter-e.m.f. by high-voltage polarisation as the current passes through the sample. This e.m.f.

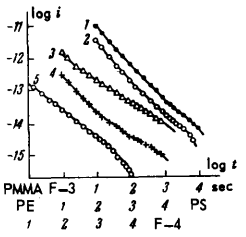


Fig. 17. The logarithm of the current flowing through a polymer as a function of time, with a constant applied voltage, at 20° [32]: 1) PMMA; 2) F-3; 3) PE_{HP}; 4) PS; 5) F-4.

decreases with an increase in the temperature, because of an increase in the diffusion [34]. It has been found for many low-molecular-weight dielectrics that the true value of the resistivity, taking this counter-e.m.f. P into account,

$$R_t = \frac{V_t - P_t}{I_t}$$

is independent of the time.

Unfortunately, all the existing data on the conductivity of polymers are not corrected for the polarisation: they refer either to the value of the current 1 min after the application of the voltage or to the "residual current". In the first case the value obtained is rather arbitrary since any period other than 1 min (suggested by the brothers Curie) could have been used. In the second case, the resistivity obtained refers to the maximum polarisation of the sample.

Information can be found in the literature about the effect of the time for which the voltage is applied, the value of the voltage, the temperature, and other factors, on the conductivity of polymers. But none of these data are corrected for the polarisation e.m.f. Moreover, the data refer to materials prepared in different ways and to different voltages applied for different lengths of time, etc. This makes it difficult to draw any general conclusions from them.

As is well known, the electrical conductivity of a substance depends on the presence in it of weakly bound or free charges, and on the mobility of these charges:

$$\kappa = \sum_t n_t e_t \lambda_t \qquad (2)$$

where n_t is the number of ions of a given type per cm^3, e_t their charge, and λ_t their mobility. It follows that factors which change these will affect the conductivity. For example, the composition and chemical structure of a polymer, temperature, and ionising radiation may all have a considerable effect on the concentration and mobility of charge carriers. Thus it has been shown that the presence in polymers of substances of low molecular weight, especially water and plasticisers, causes a considerable increase in the conductivity [35].

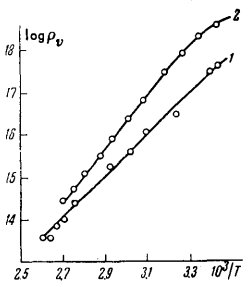


Fig. 19. The logarithm of the resistivity of PE_{LP} as a function of $1/T$: [29]: 1) ash content 0.30%; 2) ash content 0.03%;

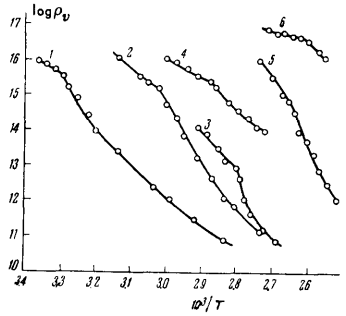


Fig. 20. $\log \rho_v = f(1/T)$ for: 1) polyvinyl acetate; 2) polyvinylbutyral; 3) polyvinylformal; 4) PMMA; 5) polyvinylethylal; 6) polystyrene [36].

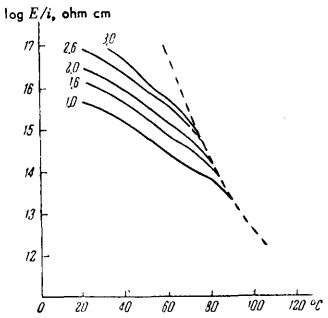


Fig. 18. The resistivity of PVC plasticised with 4.5% dioctyl phthalate, as a function of temperature. The number against each curve is the logarithm of the time [probably in seconds (Ed. of Translation)] for which the voltage was applied [33].

As has been mentioned, it is necessary to remove as far as possible from polymers traces of heterogeneous catalysts used in their preparation. These traces may decrease ρ_v.

Fig. 19 shows the logarithm of resistivity of two samples of low-pressure polyethylene taken from the same batch, but purified to different extents, as a function of the reciprocal of the absolute temperature. The first sample contains 0.3% of catalyst residue, the second 0.03%. It will be seen that the decrease in the amount of residue leads to about the same decrease in the conductivity. The temperature has a considerable effect on ρ_v.

Fig. 20 shows the logarithm of resistivity of some polymers as a function of the reciprocal of the absolute temperature [36]. It will be seen that an increase in temperature decreases ρ_v, and that there is a break in the curves near the vitrification temperature.

It has been shown [37] that, for substances of low molecular weight, the change in kinetic properties in the neighbourhood

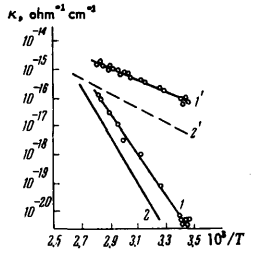


Fig. 21. The electrical conductivity of polyethylene (1) and PMMA (2) as a function of $1/T$: 1'), 2') the corresponding curves for samples irradiated with X-rays (7 to 8 r/min)[38].

of T_{vlt} is related to a sharp increase in the rate of molecular rearrangement. This may perhaps explain the break in the log ρ_v vs. $1/T$ curve, which has been observed for many polymers.

Fig. 21 shows the logarithm of the conductivity plotted against $1/T$ for samples of PE and PMMA before and during irradiation with X-rays of intensity about 7 r/min.[38] It will be seen that ionising radiation causes a considerable increase in the conductivity of polymers: for example, at room temperature the conductivity of PE increases 100 000 times. Similar results have been obtained with other polymers[38]. It is interesting to remark that on exposure to the radiation ρ_v first decreases sharply, and then slowly increases again [39,40]. Moreover, if the sample is irradiated again, it immediately assumes the conductivity it had at the end of the first irradiation. This "conditioning" of insulators is probably due to irreversible changes in the structure of the polymer caused by the irradiation, and may be of practical interest.

Even more than in the case of conductivity, the study of breakdown in polymers is complicated by the influence of factors which do not depend on the nature of the dielectric. For example, the breakdown voltage depends on the thickness and homogeneity of the dielectric, the shape of the electrodes, the atmosphere, and the frequency, wave-form, and duration of the applied voltage. By choosing standard experimental conditions, however, we can obtain a value of the breakdown voltage (E_{br}) characteristic of the polymer in question. For the purpose of establishing a relation between E_{br} and the structure of the polymer the greatest interest lies in the temperature dependence of this quantity. It is also undoubtedly of great practical value. However, we have found only a few papers dealing with this problem in the literature[41,42,43].

It seems to us that the work of Masson is the most interesting[43]. He determined E_{br} for a number of crystalline and amorphous polymers as a function of temperature, and his results are shown in Fig. 22. His measurements were carried out on samples containing a spherical cavity, and with silver or aquadag electrodes. Preliminary experiments showed that the value of E_{br} did not depend on the thickness of the sample, the rate of increase of E, the radius of the cavity, the polarity of the electrodes, or the nature of the atmosphere. It may therefore be concluded that the value of E_{br} found in these experiments is the true dielectric strength. The experiments were carried out at constant voltage.

It may be seen from Fig. 22 that as the temperature is increased, E_{br} does not vary much until the "critical" temperature is reached, after which it decreases sharply. However, in a number of cases (curve *1*, Fig. 22) there is no sharp break in the curve. The range of temperature in which E_{br} falls sharply corresponds to the melting of the polymer (PE, Fig. 22, curve *7*), or to the transition to the highly elastic state. It has been shown that the modulus of elasticity of PE and polyisobutene changes with temperature in much the same way as E_{br}, in the temperature range in which the latter shows its sharp decrease. The broken lines in Fig. 22 represent the variation of E_{br} with temperature, calculated from known values of the modulus of elasticity. There is good agreement between the experimental and calculated curves. It has therefore been concluded that the decrease of E_{br} at high temperature is probably due to the mechanical breakdown of the polymers under the influence of the electrostatic field[41,42].

The values of E_{br} given in this paper are about an order of magnitude higher than the values usually obtained by the standard methods[16]. This is obviously partly due to the quality of the polymer, and partly to the different experimental methods and conditions.

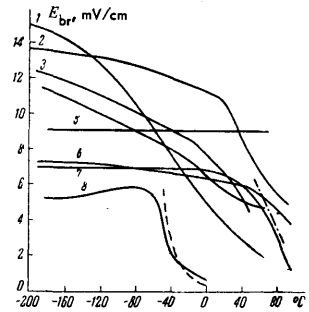


Fig. 22. The breakdown voltage of a number of polymers as a function of temperature[43]: 1) polyvinyl alcohol; 2) PMMA; 3) polyvinylchloroacetate; 4) chlorinated PE_{HP}; 5) mica; 6) PS; 7) PE_{HP}; 8) polyisobutene.

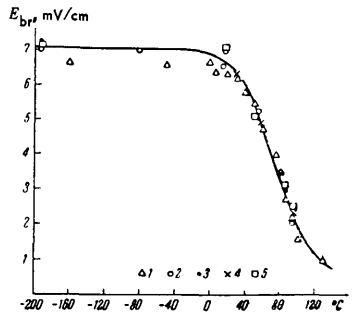


Fig. 23. The breakdown voltage of PE_{HP} as a function of temperature[42, 44-46]: 1), 2), 3), 4) unquenched samples; 5) quenched samples at 3300 Mc/s..

It may also be seen from Fig. 22 that E_{br} is higher for polar polymers than for non-polar ones. For example, comparison of curves *4* and *7* shows that the introduction of 8% of chlorine into polyethylene increases E_{br} to practically twice the value at low temperatures, although at higher temperatures the difference is no longer found.

Fig. 23 shows E_{br} for PE_{HP} as a function of temperature, as determined by a number of workers [42,44-6]. It may be seen from the figure that the values of E_{br} for quenched and slowly cooled samples are the same, i.e. the reduction of the degree of crystallinity from 60% to 50% by quenching has no effect on the breakdown voltage. However, comparison of the variation of the degree of crystallinity and the breakdown voltage with temperature shows that these two relationships are similar, which suggests that a considerable change in the degree of crystallinity would change E_{br}.

It is interesting that, as may be seen in Fig. 23, the values of E_{br} obtained at a frequency of 3.3×10^9 c/s and with direct current fall on the same curve.

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NEW STUDIES ON THE CHEMISTRY OF PROTOACTINIUM

V. A. Mikhailov

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INTRODUCTION

The existence of an element occupying the position between thorium and uranium in the Periodic System was pre-

dicted in 1871–1872 by Mendeleev[1,2], who described the chief chemical properties of the element and suggested for it the name "eka-tantalum". Protoactinium was discovered in 1918 and in the following 40 years considerable progress has been made in the study of the chemistry of this rare element*; nevertheless, protoactinium can still justifiably be regarded as one of the least studied elements. In the words of Katz and Seaborg[4], protoactinium at present enjoys "a well-deserved reputation as the most capricious and elusive of the actinide elements". The recent renewal of interest in protoactinium is due primarily to the production of large quantities of Pa^{233} during the production of U^{233} by neutron bombardment of natural thorium, and also to the continuing argument regarding the position of the start of the actinide family.

There are a number of review articles on the chemistry of protoactinium[4-12]; the most recent, by Haissinsky and Bouissieres[13], covers papers published up to the end of 1957. The present paper deals chiefly with work published during the period 1957–1958.

ISOLATION OF PROTOACTINIUM FROM NATURALLY OCCURRING SOURCES

A large proportion of the information on the chemistry of protoactinium has been obtained in the course of its isolation from naturally occurring sources, chiefly the waste residues from the production of radium or uranium. At present, the only raw material used for the isolation of protoactinium is the waste material obtained during the isolation of uranium from uranium ores, and the nature and protoactinium content of the raw material are determined by the methods used to isolate the uranium and by the uranium content of the original ore. Protoactinium is isolated, as a rule, from the waste products from the treatment of rich uranium ores and concentrates containing up to 60% U_3O_8. When radioactive equilibrium is established, 1% uranium in the ore corresponds to a protoactinium content of 3.1 mg/ton.

The behaviour of protoactinium during the isolation of the uranium depends on the type of ore, and on the nature and concentration of the acid used in the leaching process. If nitric acid alone is used, approximately half of the protoactinium present in the ore goes into solution[14,15]. During extraction by sulphuric acid or a mixture of sulphuric and nitric acids, the quantity of protoactinium dissolved increases; increase in the proportion of sulphuric acid in the mixture and a high total acidity favour the transfer of protoactinium to the solution[16,17]. Increase in the phosphorus content of the ore hinders the dissolution of protoactinium[17]. The behaviour of protoactinium during the isolation of uranium is also influenced by the presence in the ore of natural protoactinium carriers — zirconium, titanium, tantalum, and niobium.

The nature of the raw material chiefly used for the isolation of protoactinium has changed with the methods used for isolating uranium. The acid–soda method for the treatment of uranium ores was chiefly used in the initial years of the development of the atomic industry, and the protoactinium was concentrated in the so-called "carbonate residue" precipitated when the acidic solution containing the uranium was treated with excess sodium carbonate. The "carbonate residue" contained ~65% of the protoactinium in the original ore; its Pa^{231} content amount to 300–350 mg/ton.[3] The isolation of protoactinium from this type of raw material is described by Thompson and coworkers, and others[18,19]. With the development of extraction methods for the isolation of uranium, it became possible to extract protoactinium directly from the waste solutions left after the removal of uranium[20,21]. These solutions contain up to 50 mg of Pa^{231} per m^3. The protoactinium-rich precipitate obtained from these solutions at low acidity contains 100–300 mg Pa/ton and is a convenient starting material for the isolation of protoactinium[22]. The starting material of highest protoactinium content is the so-called "ethereal sludge" described below.

Since the protoactinium content of the raw material is extremely low, the first stage in the isolation is the concentration of the protoactinium into a small volume, using either extraction or precipitation methods. Extraction methods are normally used when the starting material for the isolation of the protoactinium is a solution. Extraction from nitric acid solution by tributyl phosphate is unsuitable for concentration purposes; since the efficiency is low. For example, Peppard and coworkers[21] could extract only 5–35% of protoactinium with tributyl phosphate for a 20-fold decrease in volume.

Acid esters of phosphoric acid are exceptionally powerful extracting agents for protoactinium[23,24] and their use for the extraction of protoactinium and thorium-230 (ionium) from the nitric acid solutions obtained after removal of uranium by tributyl phosphate has been described by Shevchenko and coworkers[15]. The original solution containing up to 10 mg/m^3 Pa^{231} is treated with one-twentieth of its volume of a 15% solution of a mixture of mono- and diisopentyl phosphoric acids in isopentyl acetate. The extract is washed with dilute nitric acid to remove part of the impurities extracted into the original phase, chiefly trivalent iron, after which the protoactinium is re-extracted with saturated ammonium carbonate solution. The iron remaining in the original phase after washing is also re-extracted, with the formation of soluble carbonato complexes[25]. Iron and other heavy metals are removed by precipitating their sulphides directly from the carbonate solution. The black precipitate obtained when the extract is treated with ammonium sulphide contains almost no protoactinium, which is kept in solution by the excess ammonium carbonate. (An analogous method for separating heavy metals is used in the purification of thorium[26]. The purification of protoactinium from heavy metals by precipitation of their sulphides from tartrate solution has also been decribed[27]). The ammonium carbonate is decomposed by heating and a concentrate containing up to 0.01% of protoactinium is precipitated from the filtrate. The concentrate also contains Zr, Ti, Sc, U, Th, and up to 1% of thorium-230 (ionium) from the original raw material. Approximately 85% of the original Pa and 80% of the original Th^{230} are present in the concentrate, which contains no α-emitters other than the isotopes of thorium, protoactinium, and uranium. The radiochemical purification of protoactinium thus involves merely its separation from Th^{230}, and this can be done in the usual way, for example, by treating the concentrate with dilute hydrofluoric acid and carrying out a double precipitation of thorium fluoride from the filtrate. This yields radiochemically pure Pa^{231} specimens with the α-particle energy spectrum characteristic of this isotope (Fig. 1). No attempt appears to have been made to extract Pa^{231} from such dilute solutions.

The most highly developed method is that used for the isolation of protoactinium from the ethereal sludge from the

* In 1950 the total quantitity of pure protoactinium in all the laboratories in the world amounted to only about 2 g[3].

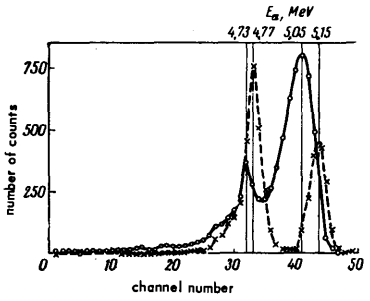


Fig. 1. α-Radiation spectrum of protoactinium-231. O — Pa^{231}; × — Np^{237} + Pu^{239}.

uranium plant at Springfield, England[17], where rich ore concentrates containing 60–70% U_3O_8 [28] are leached with a mixture of sulphuric and nitric acids, and up to 95% of the protoactinium accompanies the uranium into solution. Uranium peroxide $UO_4 . 2H_2O$ is precipitated from the resultant solution at pH 2, and carries down most of the protoactinium. The precipitate is dissolved in nitric acid and the solution extracted with ether. The dissolution is carried out at very low acidity and the resultant sludge, containing ~25% of the protoactinium present in the original raw material, is most convenient for the isolation of the element. Considerable quantities of uranium, iron, silicic acid, barium, zirconium, lead, and other impurities are also present. The protoactinium content of the sludge may amount to 3.7 g/ton, which is more than 10 times the quantity present in the carbonate residues.

The scheme illustrated in Fig. 2 has been suggested for the preliminary concentration of protoactinium, which is isolated from hydrofluoric acid solution by making use of its tendency to concentrate in the black deposit formed on sheets of aluminium metal placed in the solution. It is not yet clear whether separation of the protoactinium results from hydrolysis or from reduction to the tetravalent state.

The protoactinium is extracted from the resultant hydrochloric acid solution with two 25 litre portions of diisobutyl ketone. The combined extracts are washed with 25 litres of 8 *N* HCl and the protoactinium is re-extracted with two 2.5 litre portions of 8 *N* HCl containing HF; 2 moles $AlCl_3$ per mole HF are then added to the re-extract, and the extraction cycle is repeated: in this way, 100 kg of sludge yields 0.5 litre of a solution containing 77% of the protoactinium in the original sludge. Further purification of the protoactinium can be achieved in various ways. Good results are obtained by precipitating the protoactinium from sulphuric acid solution with hydrogen peroxide, dissolving the precipitate in 2 *N* HF, and precipitating the sparingly soluble potassium heptafluoroprotoactinate, K_2PaF_7. The Pa_2O_5 obtained in this way contains less than 1.5% of impurities, and about 1 g of Pa^{231} has been isolated by the method.

A more economical scheme has been suggested for the simultaneous isolation of uranium and protoactinium from large quantities of etheral sludge[29]. The sludge is treated in the cold with 4 *N* HNO_3 + 0.1 *N* HF; more than 95% of the protoactinium and about 99% of the uranium goes into solution. The uranium is extracted completely from the solution by 20% tributyl phosphate solution. Attempts to separate protoactinium from the purified solution by normal ion-exchange, extraction, and precipitation methods have not given good results, but it has been found that the addition of aluminium chloride, in the cold, to the purified solution gives rapid and reproducible precipitation of 85–95% of the protoactinium. It is assumed that the precipitate is formed as a result of hydrolysis and the precipitation of insoluble phosphates after the fluoride ion has been bound in a fluoroaluminate complex. This mechanism does not, however, explain why the precipitation of protoactinium is less complete when aluminium nitrate is added to the solution. Silicic acid, aluminium, and phosphorus are removed from the resultant precipitate by treating twice with concentrated caustic soda solution and washing thoroughly. The residue, which contains chiefly iron and zirconium, is dissolved in hydrochloric acid. If removal of the phosphate is incomplete, zirconium phosphate is formed during the dissolution and carries down considerable quantities of protoactinium.

Attempts to use ion-exchange methods for the further purification of protoactinium have proved unsuccessful, due to the very low capacity of the resin for Pa (~ 50 μg/g resin) in the presence of large quantities of zirconium, which leads to poor separation from this element. Further purification and concentration of protoactinium is therefore carried out by the diisobutyl ketone extraction described above. The factor for purification from Fe and Zr is over 1000, and the solution volume is reduced by a factor of 50 in 1 cycle. When the solution is left to stand, part of the protoactinium is hydrolysed, and the extraction is less satisfactory. To restore the extractability of the protoactinium, the solution is treated, before extraction, with a small quantity of HF, which is then bound with a 5-fold excess of $AlCl_3$. The hydrolysed solutions show a sharp maximum in the ultra-violet range of the absorption spectrum, at λ = 260 mμ.[30]

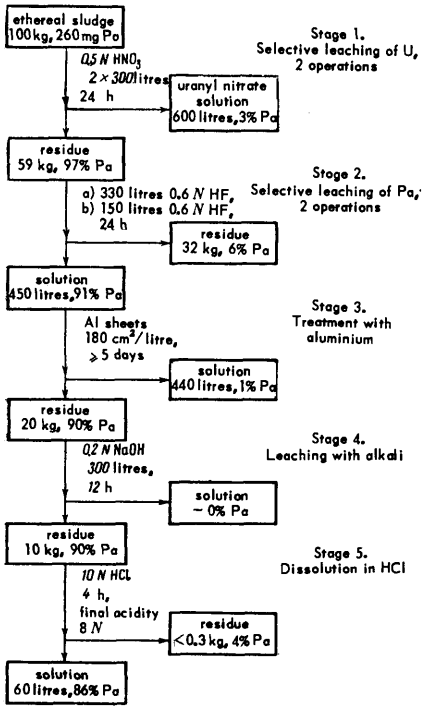


Fig. 2. Preliminary concentration of protoactinium-231[17].

The final purification of protoactinium involves 8 extraction cycles with diisobutyl ketone, adsorption from 8 *N* HCl on an anion exchange column, which is then washed with 7 *N* HCl, elution with 7 *N* HCl + 0.5 *N* HF, and precipitation of K_2PaF_7. The yield of protoactinium during the operations of the final purification is 68%.

At present the Springfield plant has ~ 50 tons of ethereal sludge, from which more than 100 g of protoactinium can be isolated[31].

The behaviour of protoactinium during the treatment of Madagascar uranothorianite ores containing ~ 40 mg/ton of protoactinium has been studied by Bouissieres and coworkers[32]. On treatment with boiling concentrated nitric acid, 65–75% of the protoactinium remains in the insoluble residue. Isolation of protoactinium from this material requires a double fusion with sodium bisulphate, which is difficult on a large scale.

ARTIFICIAL PREPARATION OF PROTOACTINIUM-231

Work on the chemistry of protoactinium is hindered by the low availability of the element. It is therefore necessary to examine briefly methods for the artificial preparation of Pa^{231}, although this subject is not directly related to the chemistry of protoactinium.

One method is by the irradiation of thorium-230 with slow neutrons, when the following reaction occurs:

$$Th^{230}(n, \gamma)Th^{231} \xrightarrow[23.5\ h]{\beta} Pa^{231}.$$

Seaborg considers that this method is more convenient than the difficult isolation of protoactinium-231 from natural sources[4,33,34]. It should be remembered, however, that the irradiated Th^{230} specimens have a high activity due to Pa^{233} and fission products. The isotopes, Pa^{233}, U^{233}, and fission products are produced as a result of the unavoidable presence of thorium-232 in the specimens.

The irradiation of Th^{230} also leads to the secondary reaction:

$$Pa^{231}(n, \gamma)\, Pa^{232} \xrightarrow[1.32\ days]{\beta} U^{232}.$$

The thermal-neutron capture cross-sections for these reactions are 50 [35] and 293 [36] barns respectively, so that on prolonged or very intense irradiation, a considerable fraction of the Th^{230} is converted to U^{232}. Our calculations show that for a flux density of 5×10^{13} neutrons $cm^{-2}sec^{-1}$ and irradiation time 10 months, 5.2% of the original Th^{230} may undergo conversion to Pa^{231}, the yield of U^{232} under these conditions being 1.1%. The maximum possible conversion of Th^{230} to protoactinium (11.8%) requires almost 5 years at the above flux density, and in the process 19.1% of the Th^{230} is converted to U^{232}.

Since the equilibrium thorium-230 content of uranium ores is more than 50 times greater than their protoactinium-231 content, this method may become important in the future, particularly since the thorium-230 enrichment of production wastes is often greater than the protoactinium enrichment. Methods for isolating thorium-230 from uranium ore residues are fairly well developed[15,21,29,37-39]. Peppard and coworkers have obtained about 66 g of thorium-230 by one of these methods[40].

Another method for the artificial preparation of protoactinium-231 is by irradiating thorium-232 with fast neutrons. At neutron energies above 6.35 MeV, the nuclear reaction is

$$Th^{232}(n, 2n)Th^{231} \xrightarrow[1.07\ days]{\beta} Pa^{231},$$

first discovered by Japanese workers in 1938[41].

Recently, as a result of the extensive use of thorium for the artificial preparation of U^{233}, it has become possible to isolate considerable quantities of protoactinium-231 from the waste products obtained after treatment of the irradiated thorium. The effective cross-section of the reaction of Th^{232} $(n, 2n)$ on irradiation with thermal neutrons depends on the relative quantity of fast neutrons in the total neutron flux and is usually 0.002–0.013 barn[42]. Calculation shows that for an integral flux of 10^{21} neutrons cm^{-2}, which corresponds approximately to irradiation with a flux of 10^{14} neutrons $cm^{-2}sec^{-1}$ for 100 days, the Pa^{231} content of the irradiated thorium amounts to 1.6–10.4 g ton^{-1}. When 1 ton of thorium is irradiated under these conditions, ~ 6 kg of thorium is converted to uranium-233, so that the yield of Pa^{231} relative to U^{233} is 0.03–0.17%. In the majority of methods used at present for treating the irradiated thorium, the Pa^{233} is isolated for the subsequent removal of the U^{233} which accumulates in it.[43] The product remaining after removal of the U^{233} should contain considerable quantities of comparatively pure Pa^{231}. It has been suggested that U^{233} will be the chief nuclear fuel of the future, so that the residue from its production may in time become an important source of Pa^{231}.

METHODS FOR DETERMINING PROTOACTINIUM

The isolation of protoactinium from natural sources and artificial products is hindered by the difficulties encountered in the quantitative determination of the element in the presence of large quantities of foreign α-emitters and macro-impurities.

For the radiochemical purification of protoactinium after separation from macro-impurities, it is convenient to coprecipitate the element with zirconium α-hydroxyphenylacetate, as proposed by Starik and coworkers[44,45]. Other useful analytical methods include extraction from hydrochloric acid solution by diisopropyl ketone and coprecipitation from HF solution with $BaZrF_6$ and BaF_2.[46] It is desirable in all cases to determine simultaneously the chemical yield of Pa^{231} by adding beforehand a known quantity of Pa^{233} to the weighed test specimen. The necessity to determine the chemical yield complicates the procedure and means that isotopic equilibrium between the different chemical forms of protoactinium must be reached.

The γ-spectrometric method for the determination of protoactinium[47], based on measurement of the activity in the Pa^{231} γ-radiation peak at an energy of ~ 300 keV, appears more promising. Foreign radio-elements do not give sharp peaks in this energy range, and after removal of Pa^{231} by treatment with hydrofluoric acid, it is easy to introduce an appropriate correction for these elements. The method makes it possible to determine reliably approximately 1.5 μg of protoactinium-231 in a 5 g sample, with an error of 1–3%. Barnett[48] has used γ-activity measurement at 300 keV for the relative determination of Pa^{231} in the absence of foreign γ-emitters.

Protoactinium-231 can be identified, and its radiochemical purity checked, using multi-channel α-analysers with

sufficiently high resolution, to record the energy spectrum of the α-particles emitted by the specimen (Fig. 1). The radiochemical purity of Pa^{231} can also be characterised fairly fully from the shape of the γ-spectrum[48].

Protoactinium-231 in natural radioactive formations in which radioactive equilibrium has been disturbed can be determined by an indirect method based on measurement of the α-activity of the daughter Th^{227}.[49] This method is of course unsuitable for the determination of Pa^{231} in materials after chemical treatment.

A recent study of the colour reactions of protoactinium with various organic ragents indicates the possibility of applying colorimetric methods to the determination of small quantities of protoactinium and for purity control[30].

Methods for the determination of Pa^{233} have been dealt with in a number of papers[50,51].

EXTRACTION OF PROTOACTINIUM BY ORGANIC SOLVENTS

Like its neighbours in the Periodic System, thorium and uranium, protoactinium is readily extracted from aqueous solutions by many organic solvents, and the use of extraction for the isolation of protoactinium from natural sources and for its subsequent purification have been described above.

The purity of the solvent is of particular importance in the extraction of protoactinium (as it is in the extraction of small or tracer quantities of other elements), since the distribution of protoactinium between the phases may be altered considerably by the presence of impurities. Thus the presence of organic peroxides in esters hinders the extraction of protoactinium from hydrochloric acid solutions[52], and extraction of the element from weakly acidic solutions by commercial tributyl phosphate is due entirely to the presence of the mono- and dibutyl phosphates[23,52]. A synergic effect is observed in the extraction of protoactinium from hydrochloric acid solutions by diisopropyl ketone–diisopropyl carbinol mixtures, i.e. there is an increase in the extracting power of the mixture compared with that of its components[52]. To avoid the adsorption of protoactinium which takes place on glass, work with the element is often carried out in polyethylene vessels, which must be treated several times before use with organic solvents to remove impurities in the polyethylene, which might otherwise be leached out gradually by the solvent and influence the extraction process[53].

Protoactinium exhibits a number of features during its extraction by organic solvents, which are not shown to the same extent by other elements. It is capable of changing from an extractable state to a non-extractable form even in 6–8 M HCl.[52] When stored in polyethylene vessels at room temperature, solutions containing protoactinium-231 can remain unchanged for several weeks, but once started, the conversion proceeds very rapidly and is complete in 1–2 days: subsequent prolonged heating with concentrated hydrochloric acid does not restore the extractability completely. Data on the extraction of partly "aged" hydrochloric acid solutions can be explained on the assumption that protoactinium exists in solution in only two forms, one of which is normally extractable while the other cannot be extracted at all. The extractable form may be a single complex or several complexes which reach equilibrium rapidly with one another. Only a normally extractable and a completely non-extractable form of protoactinium are detected in nitric acid solutions during extraction with tributyl phosphate[53]. The conversion to the non-extractable hydrolysed form in hydrochloric acid solutions is accompanied by a change in the absorption spectrum of the protoactinium[29,30]. The hydrolytic processes develop more slowly in polyethylene than in glass vessels. Protoactinium retains its ability to undergo conversion to a non-extractable colloidal form even in the organic extracts.

Best results are obtained with diisopropyl ketone in the extraction from hydrochloric acid solutions[46], but its low availability has justified the use and study of less effective extracting agents. Goble and Maddock[52] have studied the effect of the HCl concentration in the equilibrium aqueous phase on the extraction of protoactinium by the following organic solvents: diisopropyl carbinol, benzonitrile, chlorobenzene, tributyl phosphate, β,β'-dichlorodiethyl ether, nitrobenzene, *o*-nitrotoluene, *o*-nitroanisole, and a 5% solution of tributylamine in benzene. Chlorobenzene has almost no extracting action on protoactinium. The plot of the protoactinium extraction with tributyl phosphate vs. HCl concentration is a gently sloping curve, indicating its low selectivity. Nevertheless, in combination with re-extraction by a mixture of HCl + HF, extraction from hydrochloric acid solutions by tributyl phosphate has been used successfully for the separation of thorium, uranium, and protoactinium[54,55].

The ketones cyclohexanone, mesityl oxide, diethyl ketone, acetophenone, methyl n-hexyl ketone and diisobutyl ketone have been studied in more detail. For all ketones except cyclohexanone, which is completely miscible with moderately concentrated hydrochloric acid, the dependence of the distribution constant E on the mean activity of the acid, like the dependence of E on $[H^+]$ at $[Cl^-] = 5$ M and of E on $[Cl^-]$ at $[HCl] = 3$ M, is given, in logarithmic coordinates, by a family of parallel straight lines, which indicates that the mechanism of the extraction of protoactinium is the same for all these ketones. Extractable protoactinium compounds are formed at HCl concentration 3–10 M, and appear to be anionic chloro complexes. This is confirmed by the adsorption of protoactinium by anion exchange resins in this HCl concentration range. Aliphatic ketones also extract protoactinium from nitric acid solutions[56].

The extraction of protoactinium from HCl + H_2SO_4 mixtures by diisobutyl ketone has also been studied. At a constant 8 M HCl concentration , the addition of a small quantity of H_2SO_4 sharply reduces the extractability of protoactinium (from 99% to 3%), but with further increase in the H_2SO_4 concentration the extractability increases considerably. At lower HCl concentrations almost no improvement in extractability takes place with increase in the H_2SO_4 concentration. Protoactinium is extracted to a slight extent by ketones from sulphuric acid solutions, but even in 12 *N* H_2SO_4 an equal volume of diisobutyl ketone extracts only 9% of protoactinium.

Equal volumes of pentyl acetate or diisopropyl ketone extract 7% and 16% of protoactinium respectively from 1 M HCl solution 3 M with respect to ammonium thiocyanate.

Unlike tantalum and niobium, protoactinium is not extracted by methyl isobutyl ketone, even from 15 M HF.

Goble and Maddock[52] have put forward an interesting suggestion regarding the nature of the protoactinium compounds extracted from hydrochloric acid solutions. They showed that the extracting power of a solvent is directly related to its basic nature, which is in accordance with an oxonium extraction mechanism. They chose as a measure

of the basic nature the values of K_B from Gordy and Stanford[57], and the extracting power was characterised by the concentration of acid required for 50% extraction of protoactinium. The plot of the relationship between these quantities, on logarithmic coordinates, is linear, and the most basic extracting agents (cyclohexanone, mesityl oxide) extract 50% of protoactinium from weakly acidic solutions. The dependence on the basicity, together with certain other data, indicate that the solvent is associated with the cationic part of the extractable ion pair, which may be either a hydrated solvonium ion $SH^+ . aq . S$ or a solvated oxonium ion $H_3O^+ . S . aq$. This extraction mechanism shoud lead to a correlation between the extracting power of different solvents relative to different metals. Fig. 3, taken from Goble and Maddock's paper[52], shows the relationship between the distribution constants of gold and protoactinium for extraction from 8 M HCl by different solvents. For the same cationic part of the extractable ion pair, for example, in the extraction by tributylamine solutions, the extraction of protoactinium increases with increase in the dielectric constant of the solvent. Since water has the highest dielectric constant, the only ions which can be extracted are large anions whose transfer to the organic phase is accompanied by a considerable gain of energy as a result of the decrease in the work of formation of the cavity occupied by the ion.

As a rule, the extractability of protoactinium decreases with increase in its concentration*. Thus for extraction with nitrobenzene, the Pa^{231} distribution constant for an initial concentration 10^{-5} M is smaller by a factor of 30 than that found for Pa^{233} under the same conditions at an initial concentration $4-6 \times 10^{-10}$ M. For β,β'-dichlorodiethyl ether the ratio is close to 10, and for diisopropyl ketone close to 1. The increase in the distribution constant at low protoactinium concentrations is shown more clearly when the dielectric constant of the solvent is high, and can be related to the dissociation of the extractable ion pair in the organic phase. The introduction into the organic phase of a strong acid such as trifluoroacetic acid suppresses the dissociation and decreases the protoactinium distribution constant.

Moore[58] gives data for the extraction of Pa^{233} from hydrochloric acid solutions by a 5% solution of methyl di-n-octylamine in xylene. The protoactinium is extracted almost completely even from 6 M hydrochloric acid, whereas under the same conditions, only 1.2% of zirconium is extracted. Thorium does not form anionic chloro complexes and is therefore not extracted by amines. Separation from thorium and zirconium can also be achieved with more readily available amines, such as triisooctylamine. Small quantities of phosphoric acid, which prevent the extraction of protoactinium by most organic solvents, do not interfere in the extraction by a 5% solution of methyl di-n-octylamine in trichloroethylene[50].

Nikolaev and coworkers[59] have described the extraction of protoactinium salicylate by acetone in the presence of calcium chloride, which facilitates separation into layers: Zr, Th, U(VI), and Pu(IV) are also extracted. The method is suitable for the separation of protoactinium from trivalent elements, particularly the rare-earth elements.

The extraction of protoactinium from nitric acid solutions has been studied in most detail by Hardy, Scargill, and Fletcher[53], who found that when benzene solutions of tri-n-octylamine are used, the dependence of E on the HNO_3 concentration, over a wide range of the latter, corresponds to the adsorption of protoactinium by the anion-exchange resin Deacidite FF. At constant HNO_3 concentration, the protoactinium distribution constant is approximately proportional to the amine concentration in the organic phase (to the power 1), which indicates the formation, in the aqueous phase, of an anionic nitrato complex with charge -1.

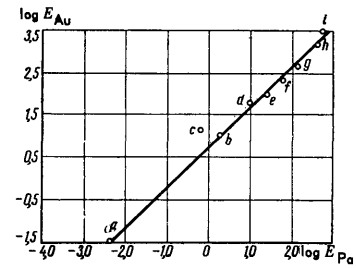


Fig. 3. Relation between distribution constants of protoactinium and gold for extraction by various organic solvents from 8 N HCl[52]. Pa^{233} concentration 5×10^{-10} M: *a*) chlorobenzene; *b*) diisopropyl ether; *c*) dibutyl phthalate; *d*) nitrobenzene; *e*) pentyl acetate; *f*) β,β'-dichlorodiethyl ether; *g*) benzaldehyde; *h*) tributyl phosphate; *i*) acetophenone.

Part of the protoactinium in nitric acid solutions, as in hydrochloric acid solutions is present in a non-extractable form. Hardy and others determined the amount of non-extractable form by the following method, first suggested by Martin[60]. If C_o and C_a are the concentrations of metal in the organic and aqueous phases respectively, and C_n the concentration of the non-extractable form, the average distribution constant of the extractable form D will be

$$D = \frac{C_o}{C_a - C_n},$$

so that

$$C_o = DC_a - DC_n .$$

Thus, if we determine the distribution of metal between the phases at different phase-volume ratios and plot C_o vs. C_a, the intercept on the C_o axis will give the value of C_n. Moreover, if equilibrium between the different complexes making up the extractable form is established rapidly, i.e. if the time taken is small compared with the time for which the phases are mixed, the plot of C_o vs. C_a will be a straight line with slope D. If this condition does not apply, the curve will be convex towards the C_o axis. In the extraction of Pa^{231} from 10^{-5} M solution in 6 M HNO_3 by a 30% solution of tributyl phosphate in kerosene, the proportion of the non-extractable form varies between 5% and 20% for different solutions. The plot of C_o vs. C_a is linear, indicating that equilibrium is established rapidly between the various nitrato-protoactinium complexes. The value of D varied from 2.2 to 3.0 in different experiments. The addition of small quantities of HF ($10^{-3}-10^{-4}$ M) decreases D sharply, but has almost no effect on the value of C_n.

The protoactinium distribution constant for extraction by tributyl phosphate solutions is approximately proportional to the square of the tributyl phosphate concentration in the

* Earlier experimental data, which indicated the higher extractability of macro-quantities of Pa^{231}, [46] have been shown to be erroneous.

organic phase. At moderate ionic strengths, maintained by adding $NaNO_3$, the protoactinium distribution constant is apparently independent of the acidity. At higher ionic strength, the relationship between the two is complex, showing a minimum value, and is analogous to the corresponding relationship for the adsorption of protoactinium by cation-exchange resins. The distribution constant also inincreases with increase in the nitrate ion concentration. Hardy and others suggest that protoactinium is extracted by tributyl phosphate as $Pa(OH)_2 . (NO_3)_3 . 2TBP$, but it is doubtful if tributyl phosphate can extract the hydroxo form. According to Gresky[61], the extractable form is $Pa(NO_3)_5 . 3TBP$.

The extraction of protoactinium by mono- and dibutylphosphoric acids was first described by Fudge and Woodhead[23], and the extraction of Pa^{233} by various alkylphosphoric acids has been studied independently and in greater detail by Shevchenko, Mikhailov, and Zaval'skii[24]. The protoactinium distribution constants are close to 1000, even when dilute dialkylphosphate solutions are used, and this should prove useful for the concentration and purification of protoactinium, particularly since these substances can extract hydrolysed and even colloidal forms of protoactinium, which are formed in solutions of low acidity and are not extracted by other solvents*[62]. The lower monoalkylphosphates are less efficient extracting agents for protoactinium.

Mikhailov, Shevchenko, and Kolganov[63] studied the influence of the extracting agent and aqueous phase composition (at an ionic strength of 6) on the efficiency of the extraction of Pa^{233} by solutions of mono- and diisopentylphosphoric acids in isopentyl acetate. The extraction process may be represented by the equilibrium

$$Pa(OH)_n A_{3\,aq}^{-} + 2HA_{org} + H_{aq}^{+} \rightleftarrows PaA_{5\,org} + 3H_2O_{aq},$$

according to which the extracting agent HA is also the complex-forming material in the aqueous phase. With increase in the acidity, the proportion of complexes of the type $Pa((OH)_n A_m^{5-n-m}$ with smaller numbers of hydroxo groups increases slightly[64]. The nitrate ion does not take part in the extraction equilibria and protoactinium can be extracted by these compounds from solutions in any mineral acid, and even from solutions containing moderately powerful complex-forming species such as $H_2C_2O_4$.[23] According to Hardy et al.[53] the extraction of protoactinium is even improved in the presence of $H_2C_2O_4$, due to the decrease in the proportion of the non-extractable polymeric form.

Although the above equation for the extraction process describes satisfactorily the available data on the extraction of tracer quantities of Pa^{233}, the actual mechanism of the process is undoubtedly much more complex, due to the extensive dimerisation of the dialkylphosphates and polymerisation of the monoalkylphosphates in the organic phase[65-68]. Moreover, these compounds can extract partly hydrolysed forms under certain conditions, as shown by Lewis and Crabtree[69] for the extraction of trivalent iron by di-2-ethylhexylphosphoric acid.

The extraction of tetravalent protoactinium has been little studied. Bouissieres and Vernois[70] found that benzene solutions of thenoyltrifluoroacetone extract Pa(IV) as $Pa(TTA)_4$ and Pa(V) as $Pa(TTA)_5$. Protoactinium(IV) is more readily extracted from hydrochloric acid solutions by thenoyltrifluoroacetone than Pa(V), but it is not extracted at all by methyl isobutyl ketone or tributyl phosphate.

* This assertion by Carleson[62] has, however, been disputed by other authors[53].

ION EXCHANGE, ADSORPTION, AND COPRECIPITATION OF PROTOACTINIUM

Protoactinium is adsorbed by strongly basic anion exchange resins from sufficiently concentrated hydrochloric acid solutions[71-74], but all the earlier data are for Pa^{233}. Goble and Maddock[52] studied the adsorption of Pa^{231} at an initial concentration $(4-6) \times 10^{-5}$ M, on Dowex 1 resin. Comparison of their data with the corresponding data for Pa^{233} obtained by other workers[71] shows that the distribution constant for the distribution of protoactinium between resin and solution increases with decrease in the protoactinium concentration, as in the extraction processes.

The ion-exchange adsorption of protoactinium from nitric acid solutions has been insufficiently studied, but Hardy and coworkers[53,75] have recently studied the adsorbability of thorium, protoactinium, and uranium from nitric acid solutions by anion and cation exchange resins. The adsorption of Pa^{231} from 10^{-5} M solutions in nitric acid on the anion exchanger Deacidite FF increases with increase in the HNO_3 concentration up to 8 M. The adsorbability of different actinides by strongly basic anion exchangers from solutions with HNO_3 concentration greater than 4 M decreases in the series

$$Np^{IV}, Pu^{IV} > Th^{IV} > Pa^{V} > U^{VI}, Np^{VI}, Np^{V}.$$

The plot of the distribution constant vs. HNO_3 concentration passes through a minimum at 3–6 M HNO_3 in the adsorption of Pa^{231} by Zeocarb 225 cation exchange resin. A minimum is also observed in the case of thorium, but that for protoactinium is much sharper. The steeper rise on the curve after the minimum in the case of protoactinium is apparently due to an increase in the average positive charge on the cation, as a result of the partial suppression of hydrolysis at higher acidity. The positive charge on the cations containing protoactinium, found from the slope of the straight line $\log D_U$ vs. $\log[HNO_3]$, is approximately 1.6. Similar values were obtained by Japanese workers[76], who used Dowex 50 cation exchange resin to separate Th^{234} (UX_1) from Pa^{234} (UX_2). The Pa^{234}, which is adsorbed in the upper part of the column together with the Th^{234}, is separated from the latter by eluting with 1–2 M HNO_3 or 0.1–0.7% oxalic acid solution. The tendency to undergo adsorption on cation exchangers from 1 M HNO_3 decreases in the series

$$Th^{IV} > Pu^{IV} > Pu^{III} > U^{VI}, Np^{VI}, Np^{V}, Pa^{V}.$$

Protoactinium-231, which forms complexes on the addition of a 1000-fold excess of HF^-, and is not extracted by tributyl phosphate, is readily adsorbed by anion exchangers, and to lesser extent by cation exchangers.

Protoactinium-231 is also adsorbed from nitric acid solutions by finely-divided graphite. For graphite powder with specific surface 68.5 m^2/g, the distribution constant is

$$\frac{\mu g\ Pa/g\ graphite}{\mu g\ Pa/ml\ solution} = 9.0 \pm 0.5.$$

The area per protoactinium atom, for the highest value of the adsorption reached (20 μg Pa/g graphite), corresponds to that of a square of side 30 Å, so that the graphite surface is far from saturated. Protoactinium is also strongly adsorbed on freshly-precipitated silicic acid and on cellulose (filter paper). The adsorption of protoactinium on silica gel is prevented by Nb, Fe(III), and Cr(III).[77]

Starik and Skul'skii[78] found that Pa^{233} is adsorbed from nitric acid solutions on fluoroplast-4 [plastic similar to

Teflon (Ed. of Translation)] and paraffin wax, which exhibit no ion-exchange properties. It is suggested that these processes involve molecular adsorption of neutral complexes of the type $[Pa(OH)_x(NO_3)_y]^0$ present in the solution. The mechanism of adsorption of protoactinium on graphite is probably similar.

Tracer quantities of Pa^{233} are readily adsorbed from nitric acid solutions on to glass, and this can be used to achieve separation from zirconium[79,80]. Starik and coworkers[81] used data on the adsorption of protoactinium by glass at different pH values to calculate the solubility product of $Pa(OH)_5$, and obtained the value 10^{-55}. The characteristic features of the adsorption and desorption of protoactinium in contact with glass indicate that ionic forms of protoactinium predominate at pH values lower than 4–4.5.

The coprecipitation of protoactinium with manganese dioxide was used long before the introduction of ion-exchange resins, and still retains its importance[59,82-85]. Lead and tin dioxides, at the moment of formation, are also able to adsorb protoactinium[86]. The adsorption of protoactinium under these conditions can probably also be regarded as molecular[78].

Nikolaev and coworkers[59] have described the coprecipitation of protoactinium-233 with various thorium precipitates and the use of the "similar-carriers" method for separating protoactinium from thorium.

Chzhaun Ya-ui[87] studied the distribution of Pa^{233} between disalicylalethylenediamine complexes of tantalum and niobium, of general formula MCl_3R_2, and their solutions in dry carbon tetrachloride. The distribution constants D were found to remain unchanged and equal to 1.6 ± 0.1 and 1.2 ± ± 0.1 in both cases respectively. The fact that D is constant indicates that the corresponding Pa, Ta, and Nb compounds are isomorphous. Isomorphous coprecipitation of Pa^{233} was not observed with the analogous titanium compounds $TiCl_2R_2$.

A number of papers have been published on the paper chromatography of protoactinium. Vernois[88] studied the influence of HCl and HF concentrations in butanol–HF–HCl–water mixtures on the relative rate of movement of protoactinium and a number of other cations along a paper chromatogram. This method can be used, with suitable choice of conditions, to effect the following separations: Pa–Ta–Nb, Pa–Ti, Pa–Bi, Pa–Fe, and Pa–Po. The separation of zirconium from protoactinium by this method is difficult[89], and in this case better results are obtained by paper electrophoresis. Lederer[90] studied the behaviour of protoactinium and its mixtures with U(VI), U(IV), Zr, and Th in the acetone–water–HCl system. The behaviour of protoactinium is altered by the presence of macro-quantities of these elements. Goble and Maddock[52] showed that when different organic solvents are used, the R_f values decrease with decrease in the extracting power.

THE STATE OF PROTOACTINIUM IN AQUEOUS SOLUTIONS

The accumulated data, obtained by different methods, on the behaviour of protoactinium, lead to some general conclusions regarding the forms in which the element exists in aqueous solutions. Most workers[53,63,64,78] favour the view that in acid solutions (at any rate in nitric acid solutions) protoactinium is present in a variety of cationic, neutral, and anionic acido complexes of the type $[Pa(OH)_nX_m]^{5-n-m}$, and that equilibrium between these forms is established rapidly. This viewpoint explains fairly satisfactorily the behaviour of protoactinium during ion exchange, adsorption, and solvent extraction.

Welch's suggestion[91] regarding the existence of the PaO_2^+ ion, analogous to the similar ions of U, Np, Pu, and Am, is difficult to reconcile with the marked differences in the chemical properties of protoactinium and the other pentavalent actinides in aqueous solutions[92]. Protoactinium shows a greater resemblance to niobium and tantalum than to the pentavalent actinides.

Most protoactinium solutions also contain macromolecular hydrolysed forms which take almost no part in the rapid equilibrium processes in the solution. At low protoactinium concentrations and high acidity, the proportion of hydrolysed form may be small, but higher protoactinium concentrations and low acidity facilitate the hydrolytic processes, as a result of which the behaviour of protoactinium at concentrations above 10^{-4} M is usually not reproducible[53].

The present author has made an approximate calculation[93] of the first acid dissociation constant of the $Pa(H_2O)_p^{5+}$ ion from the ionic potential of the Pa(V) ion, and obtained the value $10^{3\pm1}$. This high value for K_h appears to refute Elson's suggestion[5] regarding the possible existence of hydrated Pa^{5+} ions, even in strongly acidic solutions and solutions containing no complex-forming species. This value of K_h shows reasonable agreement with the stepwise acid dissociation constants of the $[PaA_3(H_2O)_3]^{2+}$ ion calculated from data for the extraction of Pa^{233} by diisopentylphosphoric acid and HA; the values were approximately 100.29 ± 5 and 21 ± 2.[64] Tracer quantities of Pa^{233} form protoactinate ions[94] in 1 N NaOH or KOH solutions, showing the weak amphoteric properties of protoactinium.

There are no quantitative data on complex-formation by protoactinium in solution. Experiments on the extraction of Pa^{231} from nitric acid solutions by tributyl phosphate in the presence of HF have given only the relative tendency of protoactinium to form complexes with the fluoride ion[53]:

$$H^+ < Fe^{3+} < UO_2^{2+} < Al^{3+} < Th^{IV} < Pa^{V} \simeq Zr^{IV}.$$

PROTOACTINIUM AND THE ACTINIDE FAMILY

The chief point in support of Seaborg's actinide hypothesis is the presence of seven 5f-electrons in curium[95]. The exact point at which the first 5f-electron appears is of less importance, in view of the proximity of the energy levels of the 5f- and 6d-electrons in the elements immediately following actinium and the possibility of a change in the electronic structure on going from one compound to another. Actinium is thus regarded as the nominal first member of the actinide family, whose members only gradually acquire features showing similarity to actinium. Thus the undeniable, though incomplete, analogies between thorium, protoactinium, and uranium and the corresponding elements in the IVA, VA, and VIA sub-groups can, in our view, be explained on the actinide hypothesis if we are not excessively rigorous with regard to terminology. Seaborg's characterisation of trans-actinium elements as elements of the 5f-6d region has been put in more concrete form by Makarov's suggestion[96,97], confirmed by extensive crystal-chemical data, regarding the dual chemical character of the first members of the actinide family.

In practice, the chemist working with protoactinium is reminded more often of its resemblance to tantalum, niobium, and zirconium than of its place in the actinide family.

The resemblance between protoactinium, zirconium, and hafnium is an example of the diagonal relationship in the Periodic Table.

The possible existence of trivalent protoactinium has not yet been confirmed. Published data on the effect which is observed in some cases in the polarographic curves, and which may be interpreted as due to the change Pa(IV)→Pa(III), are insufficiently conclusive[4,34]. The existence of lower valency states does not prove that protoactinium belongs to the actinide family, since such states are also known for tantalum and niobium.

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THE FORMATION OF TWO LIQUID PHASES IN INORGANIC SYSTEMS

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INTRODUCTION

The phenomenon of complete or partial mutual insolubility of inorganic substances in the liquid state (formation of separate layers) is encountered in various fields, such as metallurgy, glassmaking, geology, etc. Although the mechanism of separation into two or more phases has been clarified by the concept of the possible existence of microheterogeneous liquids[1], there is still no general theory of the solubility of one substance in another, nor any theory

explaining the phenomenon of partial miscibility[2-4]. The thermodynamics of binary systems, worked out by van Laar[5] and Mlodzeevskii[6] in terms of thermodynamic potential–composition diagrams, answer the question whether or not a given system will separate into two layers, but the calculation of specific thermodynamic potentials is very difficult owing to our ignorance of many thermodynamic constants. Furthermore, the thermodynamic potentials characterise only the state of a system, and give no information about the nature of immiscibility.

On this point, the view of van der Waals[7] may be regarded as generally accepted; according to this mutual insolubility in the liquid state results from a considerable difference between the intermolecular forces ("internal pressures") in the two phases. Two liquids which have similar internal pressures are miscible with one another in all proportions; when the difference in internal pressure is considerable, the liquids are completely or partly insoluble in one another. Since the internal pressure is closely linked to the macroscopic properties, such as coefficients of expansion and compressibility, surface tension, heats of vaporisation, etc., two immiscible liquids should differ markedly from one another in these macroscopic properties. The relation between phase separation and the surface tension of immiscible liquids was first demonstrated by Antonov[8], and later by other workers[9-11]. Semenchenko and Davydovskaya[2] showed experimentally, and explained in terms of the Boltzmann principle and the concept of "generalised moments", that addition of a third component which increases the surface tension of one of the liquids diminishes the mutual solubility, raising the upper and lowering the lower consolute temperatures.

The present survey attempts to systematise and generalise the considerable amount of experimental data on the formation of two liquid phases in inorganic systems (other than metallic systems); most of this has been published during the past 10–15 years.

More than 150 inorganic systems forming two liquid phases are now known and are divided into three types, AX–BY, AX–BX, and AX–AY, according to the nature of the components and the origin of the separation.

TABLE 1. AX–BY system which form two liquid phases.

	System	$\frac{P_{AX}}{P_{BY}}$	$\frac{\mu'_A}{\mu'_B}$	$\frac{\mu_A}{\mu_B}$	$\frac{\mu_X}{\mu_Y}$	Reference
1	$LiNO_3$ — AgCl			1.44	1.14	17
2	$NaNO_3$ — AgCl			1.15	1.41	17
3	KNO_3 — AgCl			0.84	1.41	18
4	$TlNO_3$ — AgCl			0.74	1.41	18
5	$Ca(NO_3)_2$ — AgCl					19
6	Li_2SO_4 — AgCl			1.44	0.81	
7	Na_2SO_4 — AgCl			1.15	0.81	18
8	Li_2WO_4 — AgCl			1.44	0.96	20
9	$LiVO_3$ — AgCl			1.44		21
10	$NaVO_3$ — AgCl			1.15		21
11	KVO_3 — AgCl			0.84		21
12	Na_2CrO_4 — AgCl			1.15		21
13	Na_2MoO_4 — AgCl			1.15		21
14	Na_2WO_4 — AgCl			1.15		21
15	$NaNO_3$ — AgBr			1.15	1.28	17
16	KNO_3 — AgBr			0.84	1.28	18
17	Li_2CrO_4 — AgBr			1.44		21
18	Li_2MoO_4 — AgBr			1.44		21
19	Li_2WO_4 — AgCl			1.44		21
20	$LiVO_3$ — AgCl			1.44		21
21	Li_2SO_4 — AgBr			1.44		21
22	Na_2CrO_4 — AgBr			1.15		21
23	Na_2MoO_4 — AgBr			1.15		21
24	Na_2WO_4 — AgBr			1.15		21
25	Na_2SO_4 — AgBr			1.15		21
26	$NaVO_3$ — AgBr			1.15		21
27	KVO_3 — AgBr			0.84		21
28	LiCl — AgI	1.26	1.82	1.44	1.22	22
29	NaCl — AgI	1.30	1.49	1.15	1.22	22
30	$NaNO_3$ — AgI			1.15	1.13	17
31	KNO_3 — AgI			0.84	1.13	23
32	$TlNO_3$ — AgI			0.76	1.13	24
33	KNO_3 — TlBr			1.12	1.28	25
34	Na_2SO_4 — TlBr			1.52	0.75	26
35	KNO_3 — TlI			1.12	1.13	18
36	Li_2SO_4 — $CdCl_2$			0.66	0.81	27
37	Li_2CrO_4 — $CdBr_2$			0.63		21
38	CsCl — LiF	0.99	2.16	2.10	1.36	28
39	CsBr — LiF	0.96	2.22	2.10	1.47	28
40	$PbCl_2$ — Ag_2S	1.76	1.04	0.59	0.48	29
41	Li_2SO_4 — $PbCl_2$			0.85	0.81	30
42	LiF — PbO	3.30	2.57	0.85	2.03	
43	NaF — PbO	3.34	2.06	0.68	2.03	21,31
44	KCl — PbO	3.20	1.45	0.50	2.79	21
45	NaCl — PbO	3.10	1.93	0.68	2.79	21
46	RbCl — PbO	3.22	1.32	0.44	2.79	21
47	NaBr — PbO	2.96	1.50	0.68	3.00	21
48	KF — PbO	3.40	1.26	0.50	2.03	21
49	KBr — PbO	3.10	1.41	0.50	3.00	21
50	KI — PbO	3.00	1.36	0.50	3.50	21
51	Li_2SO_4 — PbO			0.85	2.25	21
52	Na_2SO_4 — PbO			0.68	2.25	21
53	K_2SO_4 — PbO			0.50	2.25	21
54	Li_2WO_4 — PbO			0.68	2.69	21
55	Na_2WO_4 — PbO			0.68	2.69	21
56	K_2WO_4 — PbO			0.50	2.69	21
57	Na_2CrO_4 — PbO			0.68	2.25	21
58	Na_2MoO_4 — PbO			0.68	2.69	21
59	K_2MoO_4 — PbO			0.50	2.69	21
60	Na_2CrO_4 — PbO			0.68	2.25	21
61	Na_2MoO_4 — PbO			0.68	2.69	21
62	K_2MoO_4 — PbO			0.50	2.69	21
63	K_2CrO_4 — PbO			0.50	2.69	21
64	Li_2CO_3 — PbO			0.85	1.96	21
65	Na_2CO_3 — PbO			0.68	1.96	21
66	K_2CO_3 — PbO			0.50	1.96	21
67	Na_2TiO_3 — PbO			0.68		21
68	K_2TiO_3 — PbO			0.50		
69	NaCl — B_2O_3	1.63	9.00	0.07	2.79	
70	KCl — B_2O_3	1.67	11.9	0.05	2.79	
71	Na_2SO_4 — B_2O_3			0.07	2.25	
72	NaCl — TiO_2	2.30		0.16	2.79	
73	KCl — TiO_2	2.37		0.12	2.79	
74	CaS — SiO_2			0.19	1.33	32
75	FeS — SiO_2	0.30	1.33	0.30	1.33	32
76	MgF_2 — SiO_2			0.25	0.5	33,34
77	CaF_2 — SiO_2			0.18	0.5	33,34
78	SrF_2 — SiO_2			0.15	0.5	33,34
79	BaF_2 — SiO_2			0.14	0.5	33,34
80	KCl — $Na_2B_4O_7$*			0.7		35
81	NaCl — $K_2B_4O_7$			0.7		35
82	NaF — $PbTiO_3$*			0.68		31
83	$LiSO_4$ — V_2O_5					
84	$CaSO_4$ — $Na_2B_4O_7$*			0.5		36
85	Na_2MoO_4 — $PbTiO_3$*			0.68		
86	K_2MoO_4 — $PbTiO_3$*			0.50		37
87	Na_2CO_3 — $PbTiO_3$*			0.68		
88	K_2CO_3 — $PbTiO_3$*			0.50		
89	K_2CO_3 — $PbZrO_3$*			0.50		
90	Na_2CO_3 — $PbZrO_3$*			0.68		

I. AX–BY SYSTEMS

Diagonal Sections (Composition Squares) of Reciprocal Ternary Systems

Table 1 gives all known AX–BY systems which separate into two liquid phases. For some of them values are given for the relative polarities of the compounds AX and BY*, the relative generalised ionic moments** μ_A/μ_B and μ_X/μ_Y [12,13], and the relative generalised moments of the cations μ'_A/μ'_B corrected for the effective charges on the ions.

All AX–BY systems can be divided into two groups, according to the manner in which layers are formed. Group (*a*) comprises systems in which two layers are formed in consequence of the mutual insolubility of the components AX and BY in the liquid state. In these systems a solid phase (the more infusible component) is in equilibrium with two liquids consisting mainly of component AX and component BY respectively. Group (*b*) comprises systems in which the cause of separation is not the complete or partial mutual insolubility of the molten components, but the decomposition of one of the components, e.g. BY, on melting, one of the resulting products being immiscible with molten AX. In these systems the solid phase is in equilibrium with two liquids consisting mainly of AX and a decomposition product of BY respectively.

Systems Ia. Among the ninety systems in Table 1, eighty (without asterisks) are Ia systems. They represent stable pairs of compounds of the corresponding reciprocal ternary systems A, B || X, Y, consisting either of simple compounds of the type of halides, oxides, sulphides, etc. (and therefore not triangulating sections of more complex systems), or else of a pair of simple compounds (halides, oxides, sulphides, etc.) and a pair of complex salts (nitrates, carbonates, sulphates, etc., predominantly of the alkali metals), and are therefore triangulating sections of more complex four-component systems involving six compounds A, B, C || X, Y (Fig. 1).

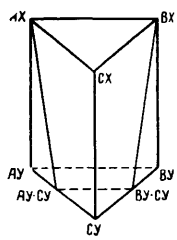


Fig. 1.

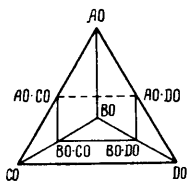


Fig. 2.

A survey of Ia systems, taking into account the characteristics of the components and the ions which they contain, allows several generalisations to be made about the conditions necessary for separation to occur.

From Table 1 the following conditions appear to be necessary for the formation of layers in AX–BY systems: one of the components must be a simple compound of comparatively low polarity* or a halide, an oxide, or a sulphide, etc. of a metal which yields a cation having an outer electron shell differing in structure from that of an inert gas (lead, thallium, silver, etc.), or even an acid anhydride B_2O_3, TiO_2, V_2O_5, etc; the other component is a typical salt, a halide, sulphate, nitrate, carbonate, etc., mainly of an alkali metal (only two systems are exceptions: LiF–CsCl and LiF–CsBr). Hence the compounds AX and BY should differ markedly from one another *in polarity*, and the two cations A and B must have electron shells of *different* structure, and differ markedly from one another in polarity [30] and generalised moments, and the corresponding atoms should differ in electronegativity. The anions X and Y should differ markedly from one another in their generalised moments, structure, valency, composition, and, if they are simple ions, in the electronegativity of their atoms.

These conditions do not contradict the effects noted earlier favouring the formation of layers [2,9–11,30].

Systems Ib. Only ten Ib systems are known (denoted by asterisks in Table 1). Three of these (Nos. 80–82) are diagonal sections of reciprocal ternary systems which are unstable sections of the prism formed by the six compounds A, B, C || X, Y (Fig. 1); the remaining systems are diagonal sections of reciprocal ternary systems which are unstable sections of tetrahedra representing the four oxides A, B, C, D || O (Fig. 2). One of the components of these systems, e.g. BY ($Na_2B_4O_7$, $PbTiO_3$, $PbZrO_3$) fuses with decomposition under the influence of the component AX. The decomposition product (B_2O_3, PbO) is not miscible with the component AX in the liquid state. This is readily seen from a more detailed examination of the systems Na, Pb || F, TiO_3 [31], Na, K || Cl, B_4O_7 [35], and Na, Ca || SO_4, B_4O_7 [36], which are sections of the corresponding prisms Na, Pb, Ti || O, F and Na, K, B || O, Cl (Figs. 3*a* and 3*b*) and the tetrahedron Na, Ca, B, S || O.

In the first system a small region of two liquid phases can be observed in the NaF–$PbTiO_3$ section adjacent to the NaF component. Separation occurring in the NaF–PbO lateral system (stable diagonal of the Na, Pb || F, O face of the prism in Fig. 3*a*), extending inside the prism in the plane of the NaF–PbO–TiO_2 triangle, covers only part of the NaF–$PbTiO_3$ section (Fig. 4) [31], which indicates that the Na, Pb || F, TiO_3 section of the Na, Pb, Ti || F, O prism is unstable in the liquid state. One of the two liquid phases in equilibrium with the solid phase consists mainly of sodium fluoride, and the other predominantly of lead oxide formed by the decomposition of lead titanate, which forms the solid phase. This means that lead titanate decomposes at a lower temperature (900°–950°) in molten sodium fluoride than in the pure state (1124°) [38].

In the Na, K || Cl, B_4O_7 system neither of the diagonal sections NaCl–$K_2B_4O_7$ and KCl–$Na_2B_4O_7$ can be stable, since other portions of the system, in this case the sides of the NaCl–$Na_2B_4O_7$ and KCl–$K_2B_4O_7$ composition squares,

* The poliarities P_{AX} and P_{BY} were calculated by Nekrasov's method [14, 15], and their values have been published [16].

** According to Semenchenko, the generalised moment of an ion is calculated by dividing its valency by its radius: $\mu = Z/r$.

The corrected generalised moment of a cation is calculated by dividing its effective charge by its radius: $u' = e/r$.

* The term "low polarity" is used in the sense of a considerable deviation from a purely ionic bond.

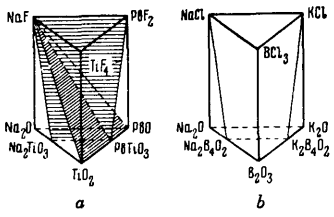


Fig. 3.

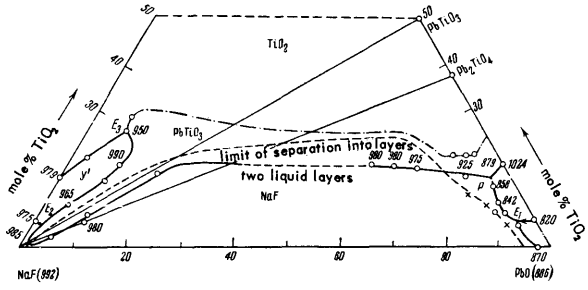


Fig. 4.

In the $Na_2B_4O_7-CaSO_4$ system [36], as in the preceding case, separation into layers is a consequence of the mutual insolubility of sodium and calcium sulphates in the boric anhydride formed by the decomposition of sodium and calcium tetraborates.

In the $Na_2CO_3-PbTiO_3$, $K_2CO_3-PbTiO_3$, $K_2MoO_4-PbTiO_3$, $NaCO_3-PbZrO_3$, and $K_2CO_3-PbZrO_3$ systems, which form parts of the corresponding tetrahedra Na(K), Pb, Ti(Zr), Mo(C) || O, separation into layers is due to decomposition of lead titanate or zirconate into lead oxide and the corresponding dioxide; lead oxide, sodium and potassium carbonates, and potassium molybdate are almost completely insoluble in one another. A diagram of the $K_2CO_3-PbTiO_3$ system shows clearly (Fig. 6) that separation into layers arising at the K_2CO_3-PbO side extends inside the triangle, covering the $K_2CO_3-PbTiO_3$ section. In this system, as in the $NaF-PbTiO_3$ one, lead titanate decomposes under the influence of potassium carbonate at 850°–900°, which is lower than with the pure compound.

It is clear from this brief survey of AX–BY systems that immiscible liquid phases are formed, independently of the complexity of the components, when one component is a simple compound of low polarity, typified by the halides, oxides, sulphides, etc. of metals whose cations do not have an inert gas structure (lead, silver, cadmium, thallium, etc.), or an acid anhydride (B_2O_3, V_2O_5, TiO_2). If neither of the components AX and BY is a compound of the above type, separation occurs only when such a compound is formed by decomposition of one of the components.

are unstable sections of other, more complex systems (in this case the faces of the prism, Fig. 3*b*), and hence the Na, K || Cl, B_4O_7 system itself is an unstable section of the prism in Fig. 3*b*, as is clear from the known principles relating to stable portions of complex systems [26]. That the $NaCl-Na_2B_4O_7$ and $KCl-K_2B_4O_7$ are unstable sections of the corresponding reciprocal ternary systems Na, B || Cl, O and K, B || Cl, O (faces of the prism in Fig. 3*b*) can be judged firstly from the data of Harrison [66], who showed cryoscopically that sodium tetraborate in molten sodium chloride is partly dissociated according to the equation

$$Na_2B_4O_7 = 2Na^+ + O^{2-} + 2B_2O_3;$$

and secondly by comparing the miscibility of sodium and potassium borates with that of boric anhydride in molten sodium and potassium chlorides respectively. The solubility of sodium and potassium chlorides in boric anhydride is considerably less than in the corresponding tetraborates [37], which is well shown for the sodium systems in Fig. 5, where data for part of the $NaCl-Na_2B_4O_7-B_2O_3$ ternary system are given. It is clear that $NaCl-B_2O_3$ forms a stable section of the reciprocal system, whereas the $NaCl-Na_2B_4O_7$ section is of subordinate importance, like, for example, the sections $4AgI.KI-KNO_3$, $KNO_3.KI-AgI$, or $AgNO_3.AgI-KNO_3$ and $2AgNO_3.AgI-KNO_3$ in the K, Ag || I, NO_3 system studied by Dombrovskaya and Koloskova [23]. Hence separation in $NaCl-Na_2B_4O_7$ and $KCl-K_2B_4O_7$ is a result not of immiscibility of the components but of a more complex interaction.

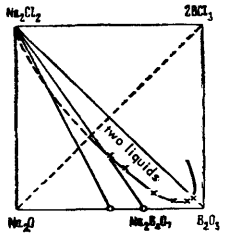


Fig. 5.

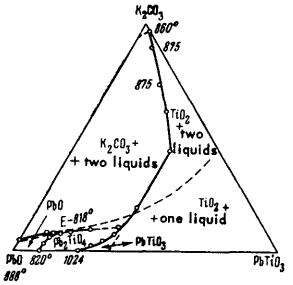


Fig. 6.

II. AX–BX SYSTEMS

All the AX–BX systems known to form immiscible liquid phases are listed in Table 2.

In these AX–BX systems one of the compounds (BX) is of low polarity and formed by a cation bearing three or four charges (B = Al, Si, B, Sb), while the other compound is a typical salt or basic oxide of a uni- or bivalent metal. Only in the $SbCl_3-SnCl_4$ system are both components of low polarity and non-saltlike. In all the systems the relative characteristics of the A and B ions favour separation into

TABLE 2. AX—BY systems which form two liquid phases.

No.	System	Compounds formed in systems	Solid phase in equilibrium with the two liquids	Reference
1	$NaBr - AlBr_3$	$NaBr \cdot AlBr_3$; $NaBr \cdot 2AlBr_3$ $2NaBr \cdot 7AlBr_3$; $x\ NaBr \cdot y\ AlBr_3$	$x\ NaBr \cdot y\ AlBr_3$	39
2	$KBr - AlBr_3$	$KBr \cdot AlBr_3$; $KBr \cdot 2\ AlBr_3$ $x\ KBr \cdot y\ AlBr_3$	$x\ KBr \cdot y\ AlBr_3$	40
3	$NH_4Br - AlBr_3$	$NH_4Br \cdot AlBr_3$; $NH_4Br \cdot 2\ AlBr_3$ $NH_4Br \cdot 3\ AlBr_3$; $x\ NH_4Br \cdot y\ AlBr_3$	$x\ NH_4Br \cdot y\ AlBr_3$	40
4	$AgBr - AlBr_3$	$AgBr \cdot AlBr_3$; $AgBr \cdot 2\ AlBr_3$	$AgBr \cdot 2AlBr_3$	40
5	$CaBr_2 - AlBr_3$	$CaBr_2 \cdot AlBr_3$; $x\ CaBr_2 \cdot y\ AlBr_3$	$x\ CaBr_2 \cdot y\ AlBr_3$	39,41
6	$BaBr_2 - AlBr_3$	$BaBr_2 \cdot 2\ AlBr_3$	$BaBr_2 \cdot 2\ AlBr_3$	40
7	$Hg_2Br_2 - AlBr_3$	$Hg_2Br_2 \cdot 2\ AlBr_3$	$Hg_2Br_2 \cdot 2\ AlBr_3$	40
8	$TlBr - AlBr_3$	$TlBr \cdot AlBr_3$; $TlBr \cdot 2\ AlBr_3$ $x\ TlBr \cdot y\ AlBr_3$	$x\ TlBr \cdot y\ AlBr_3$	40
9	$SnBr_2 - AlBr_3$	$SnBr_2 \cdot AlBr_3$; $SnBr_2 \cdot 2\ AlBr_3$;	$SnBr_2 \cdot 2\ AlBr_3$	40
10	$PbBr_2 - AlBr_3$	$PbBr_2 \cdot 2\ AlBr_3$	$PbBr_2 \cdot 2\ AlBr_3$	40
11	$NaCl - AlCl_3$	$NaCl \cdot AlCl_3$; $x\ NaCl \cdot y\ AlCl_3$	$x\ NaCl \cdot y\ AlCl_3$	40
12	$KCl - AlCl_3$	$KCl \cdot AlCl_3$; $x\ KCl \cdot y\ AlCl_3$	$x\ KCl \cdot y\ AlCl_3$	40
13	$NH_4Cl - AlCl_3$	$NH_4Cl \cdot AlCl_3$; $x\ NH_4Cl \cdot y\ AlCl_3$	$x\ NH_4Cl \cdot y\ AlCl_3$	40
14	$AgCl - AlCl_3$	$AgCl \cdot AlCl_3$; $x\ AgCl \cdot y\ AlCl_3$	$x\ AgCl \cdot y\ AlCl_3$	40
15	$BaCl_2 - AlCl_3$	$BaCl_2 \cdot 2AlCl_3$	$BaCl_2 \cdot 2\ AlCl_3$	40
16	$TlCl - AlCl_3$	$TlCl \cdot AlCl_3$; $TlCl \cdot 2\ AlCl_3$ $x\ TlCl \cdot y\ AlCl_3$	$x\ TlCl \cdot y\ AlCl_3$	40
17	$SnCl_2 - AlCl_3$	$SnCl_2 \cdot AlCl_3$; $SnCl_2 \cdot 2AlCl_3$ $xSnCl_2 \cdot yAlCl_3$	$x\ SnCl_2 \cdot y\ AlCl_3$	40
18	$SnCl_2 - SbCl_3$	$xSnCl_2 \cdot ySbCl_3$	$x\ SnCl_2 \cdot y\ SbCl_3$	40
19	$SbCl_3 - SnCl_4$	—	$SbCl_3$	40
20	$SrO - SiO_2$	$2SrO \cdot SiO_2$; $SrO \cdot SiO_2$	SiO_2	41,42
21	$CaO - SiO_2$	$2CaO \cdot SiO_2$; $3\ CaO \cdot 2\ SiO_2$; $CaSiO_3$	SiO_2	42,43
22	$MgO - SiO_2$	$2\ MgO \cdot SiO_2$; $MgO \cdot SiO_2$	SiO_2	43
23	$ZnO - SiO_2$	$2ZnO \cdot SiO_2$	SiO_2	43
24	$FeO - SiO_2$	$2FeO \cdot SiO_2$	SiO_2	44
25	$MnO - SiO_2$	$2\ MnO \cdot SiO_2$; $MnO \cdot SiO_2$	SiO_2	43
26	$Cu_2O - SiO_2$		SiO_2	45
27	$BaO - B_2O_3$	$3BaO \cdot B_2O_3$; $BaO \cdot B_2O_3$; $BaO \cdot 3\ B_2O_3$	$BaO \cdot 3\ B_2O_3$	43
28	$CaO - B_2O_3$	$3CaO \cdot B_2O_3$; $CaO \cdot 2B_2O_3$; $CaO \cdot B_2O_3$; $CaO \cdot 3B_2O_3$	$CaO \cdot 3\ B_2O_3$	43
29	$MgO - B_2O_3$	$3MgO \cdot B_2O_3$; $2\ MgO \cdot B_2O_3$; $MgO \cdot B_2O_3$	$MgO \cdot B_2O_3$	46
30	$ZnO - B_2O_3$	$5ZnO \cdot 2\ B_2O_3$; $ZnO \cdot B_2O_3$	$ZnO \cdot B_2O_3$	47
31	$CdO - B_2O_3$	$3CdO \cdot B_2O_3$; $2CdO \cdot B_2O_3$; $3CdO \cdot 2B_2O_3$; $2CdO \cdot 3\ B_2O_3$	$2\ CdO \cdot 3\ B_2O_3$	48
32	$PbO - B_2O_3$	$4\ PbO \cdot B_2O_3$; $2\ PbO \cdot B_2O_3$; $5PbO \cdot 4\ B_2O_3$; $PbO \cdot 2\ B_2O_3$	$PbO \cdot 2\ B_2O_3$	49
33	$CoO - B_2O_3$	$3CoO \cdot B_2O_3$; $2CoO \cdot B_2O_3$; $xCoO \cdot yB_2O_3$	$x\ CoO \cdot y\ B_2O_3$	50,51
34	$Na_2S - Ni_2S$	—	Ni_2S	8
35	$Na_2S - Ni_2S_3$	—	Ni_2S_3	18
36	$Na_2TiO_3 - K_2TiO_3$	$2\ Na_2TiO_3 \cdot K_2TiO_3$	$2\ Na_2TiO_3 \cdot K_2TiO_3$	52
37	$UF_6 - HF$	—	UF_6	53
38	see also $M^{I}Cl - M^{V}Cl_5$ systems			54

layers and also[55-58] the formation of complex compounds of the type $nAX.mBX$. In fact, as can be seen from Table 2, in most cases complex formation occurs as well as separation. Although these two phenomena would seem to be mutually exclusive (since the tendency to complex formation is known always to increase the mutual solubility of the components), the activity coefficient of a dissolved salt in systems exhibiting complex formation is always less than unity and, as Voskresenskaya[55] has shown, the real solubility curve (the primary crystallisation curve) lies below the ideal curve calculated from Shreder's equation[59].

On the other hand, it is also known that a "tendency" to separate into two phases (or actual separation) appears when the real solubility curve lies above the ideal curve, and the activity coefficient of the salt which crystallises is greater than unity in the melt. It is easily seen, however, that in the overwhelming majority of systems separation is a consequence of the complete or partial mutual insolubility not of the components AX and BX but of the compound $nAX.mBX$ and the less polar component BX. The liquidus curves for several AX—BX systems show that separation occurs adjacent to the less polar components $AlBr_3$, $AlCl_3$, B_2O_3, and SiO_2. Between the heterogeneous region and the ordinate of the more polar component (NaBr, NaCl, KBr, KCl, CaO, MgO, BaO, etc.) one or more compounds of the type $A_n[B_mX_{nm}]$ appear. Part of the BX—$A_n[B_mX_{nm}]$ system can be regarded as an independent system of the AX—BY type having four different ions — A, B, X, and $[B_mX_{nm}]$. Thus the formation of complex compounds in AX—BX systems produces favourable conditions for separation owing to the nature of the anions. Actually the pair of anions X and $[B_mX_{nm}]$ satisfy all the conditions favouring separation enumerated in section I. It is also evident from Figs. 7—9 that in many AX—BX systems exhibiting complex formation and phase separation the temperature of the three-phase monotectic process is below the melting point of the complex compound, which makes it certain that separation is due to the mutual insolubility of the complex and BX, that the former does not dissociate into its components at the temperature at which separation occurs, and that one of the liquid phases consists mainly of the molten complex compound. The two liquid phases are here in equilibrium either with the solid compound $A_n[B_mX_{nm}]$, of its melting point is above that of the component BX, or with the solid BX phase, if the converse is true. Among real systems of the latter type are $AlBr_3$—AgBr, $-BaBr_2$, $-Hg_2Br_2$, $-SnBr_2$, and $-PbBr_2$, and $AlCl_3-BaCl_2$, $SrO-SiO_2$, $CaO-SiO_2$, $MgO-SiO_2$, $BaO-B_2O_3$, $CaO-B_2O_3$, $MgO-B_2O_3$, and $PbO-B_2O_3$.

In systems of this kind it quite often happens that the resulting complexes decompose on fusion into two immiscible liquids, one of which consists mainly of BX, and the other of either another complex compound or the component AX, if the latter is of low polarity. Representatives of the

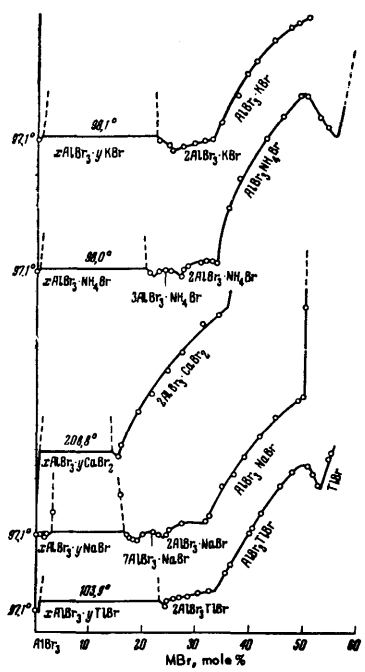


Fig. 7.

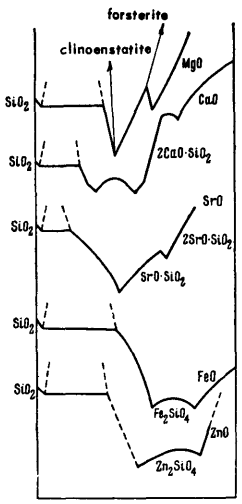


Fig. 8.

former are the systems $AlBr_3-Na(K, NH_4, Tl, Ca)Br$, $AlCl_3-Na(K, Ag, NH_4, Tl)Cl$, and $CoO-B_2O_3$, and the latter are represented by the $SnCl_2-SbCl_3$ system. Such systems are of interest firstly because they have hitherto been regarded as rare exceptions among metallic and organic systems[3], and secondly because the $SnCl_2-SbCl_3$ system provides a good example of conditions for the formation of two phases and of complexes being very similar: depending on the temperature, either two phases or a complex compound are formed. The complex $x SnCl_2.y SbCl_3$ exists only up to a temperature of 243.1°, when it decomposes into the immiscible components $SnCl_2$ and $SbCl_3$. The same type includes also a few silicate systems, e.g. $FeO-SiO_2$ and $MnO-SiO_2$, in which the compounds formed melt incongruently, without reaching the temperature at which immiscible liquids are formed.

On the above basis inorganic AX–BX systems which form two liquid layers can be classified as follows (Fig.10):

1. Systems formed by two non-saltlike compounds of low polarity, of either semi-closed or closed type (in Kossel's sense); the cations A and B bear three or more charges; no complex compounds are formed. Separation is a consequence of complete or partial mutual insolubility of AX and BX due to a sharp difference in the intermolecular cohesive forces in the components. The two liquid phases are in equilibrium with a solid phase formed by the higher-melting component. The $SbCl_3-SnCl_4$ system is an example.
2. Systems consisting of pairs of compounds AX and BX, one of which is like those in systems of group 1, while the other is saltlike, but the resulting cations do not have the inert gas type of electron shell, e.g. FeO, MnO, $SnCl_2$. The relative characteristics of the cations A and B favour both separation into two phases and complex formation, but the complexes formed melt (*a*) with decomposition, without reaching the temperature at which two phases are formed ($FeO-SiO_2$, $MnO-SiO_2$), or (*b*) with decomposition into two immiscible liquids ($SnCl_2-SbCl_3$). In both cases the solid phase in equilibrium with the two liquid phases consists of the higher-melting component.
3. Systems composed of pairs of compounds AX and BX, one of which is of the low-polarity type of $AlCl_3$, SiO_2, B_2O_3, etc., and the other is a typical salt of a uni- or bivalent metal or else an oxide of a bivalent metal. One or several complex compounds are formed in the systems. The formation of separate phases is here a consequence of the mutual insolubility of the complex and the low-polarity component; the two liquid layers are in equilibrium with a solid phase consisting of either the complex compound or the component BX, depending on their melting points. The complex compound in equilibrium with the two liquids either has the same composition in the liquid and solid state (Fig. 10, 3*a* and 3*d*) or else decomposes on melting into a complex of different composition and the component BX, when the solid and liquid phases of the compounds differ in composition (Fig. 10, 3*c*).

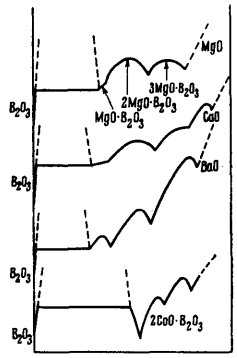


Fig. 9.

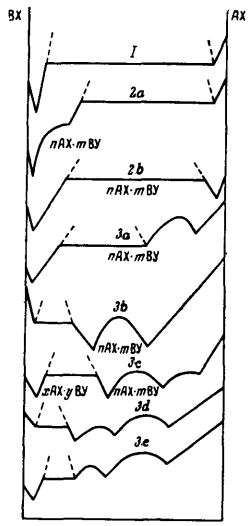


Fig. 10.

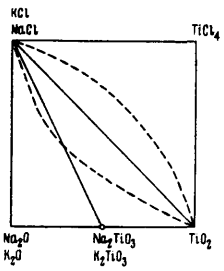


Fig. 11.

Somewhat different from these AX–BX systems is the $Na_2TiO_3-K_2TiO_3$ system, which contains the same anion and cations having very similar characteristics. According to Nisioka's data[60], two liquid phases are formed over the range 50–80 mole % Na_2TiO_3. According to the careful investigations of Sholokhovich[52], separation into two phases and compound formation both occur in this system.

This view of the formation of immiscible phases in AX–BX systems agrees with Esin's generally accepted hypothesis[1] of the microheterogeneity of liquids due to the formation, especially in silicate systems having low MO contents, of cybotactic groups approximating in composition to MO and to SiO_2. From electrostatic considerations and the shape of the property–composition diagrams, however, the cybotactic groups in silicate systems leading to microheterogeneity of the melt should evidently have a different composition. At low MO concentrations, where two liquid phases occur in silicate systems, cybotactic groups approximating to MO in composition are absent, since the oxygen of the MO is completely transferred to the silica, forming MSi_xO_y cybotactic groups; the part of the silica not required in the Si_xO_y ion forms cybotactic groups approximating to SiO_2 in composition. Formation of these groups determines the microheterogeneity of the melt and thus its separation into layers. A similar mechanism occurs also in $AlHal_3$–MHal systems.

III. AX–AY SYSTEMS

Table 3 lists the seventeen AX–AY systems known to us which form two liquid phases.

In the first two systems the separation has the same character as in AX–BX systems (Fig. 10, 3*c* and Fig. 11). The compounds $HCl.H_2O$ and $HBr.H_2O$ decompose on fusion into two immiscible liquids according to the equations

$$2(HCl.H_2O) = HCl.2H_2O + HCl,$$

$$2(HBr.H_2O) = HBr.2H_2O + HBr.$$

The two liquid phases are here in equilibrium with the compounds $HCl.2H_2O$ and $HBr.2H_2O$.

The remaining fifteen systems are composed of typical salts of sodium and potassium with various anions. In all these systems one of the salts is a silicate, titanate, or tetraborate. The fact that both components of these AX–AY systems (apart from the first two) are salts of the same alkali metal does not favour separation, but it does occur in these systems. How does it originate? Is it a consequence of the mutual insolubility of the components AX and AY due to a marked difference in properties of the anion pairs Cl and B_4O_7, SO_4 and B_4O_7, MoO_4 and TiO_3, SO_4 and TiO_3, etc., or of the formation of a complex compound immiscible with one component, or even because of these systems being unstable sections of more complex systems one of whose components is immiscible with the component AX? It is evidently necessary to take all three possibilities into account. But one of the components in all the systems (apart from 1 and 2) in Table 3 is an alkali-metal titanate, silicate, or tetraborate, which on fusion with other salts are converted into more acid or more basic forms; systems containing them are thus often unstable sections of more complex systems[64] and the third possibility is the most probable. In fact, as has already been shown, the $NaCl-Na_2B_4O_7$, $KCl-K_2B_4O_7$, and $Na_2SO_4-Na_2B_4O_7$ systems form subsections of the corresponding reciprocal ternary systems, and here the formation of immiscible liquids cannot be considered apart from these reciprocal systems (Fig. 5). Similarly, the $NaCl-Na_2TiO_3$ and $KCl-K_2TiO_3$ systems form unstable portions of the reciprocal ternary systems Na(K), Ti ‖ Cl, O, as is clear from Fig. 11.

TABLE 3.

1. HCl — H_2O[61]	7. KCl — K_2TiO_3[63]	13. Na_2WO_4—Na_2TiO_3[63]
2. HBr — H_2O[61]	8. NaCl — Na_2TiO_3[63]	14. K_2WO_4—K_2TiO_3[63]
3. NaCl — $Na_2B_4O_7$[25]	9. K_2WO_4— K_2TiO_3[63]	15. Na_2MoO_4— Na_2SiO_3[62]
4. KCl — $K_2B_4O_7$[25]	10. Na_2SO_4 — Na_2TiO_3[63]	16. Na_2CrO_4— Na_2TiO_3[63]
5. Na_2SO_4— $Na_2B_4O_7$[26]	11. K_2SO_4— K_2TiO_3[63]	17. K_2CrO_4— K_2TiO_3[63]
6. K_2WO_4— K_2SiO_3[62]	12. Na_2MoO_4— Na_2TiO_3[63]	

Hence in seven of the seventeen AX–AY systems in Table 3 partial miscibility is associated either with complex formation (the first two) or with the systems representing unstable portions of more complex systems. In the remaining ten systems the origin of the separation has not yet been ascertained; it is evidently the same as in systems of chlorides with sodium and potassium tetraborates and titanates, and of sodium sulphate with sodium tetraborate.

CONCLUSION

This review leads to the following general propositions concerning the conditions necessary for immiscible liquid phases to be formed in inorganic systems:

1. All AX–BY, AX–BX, and AX–AY systems can form two liquids when both components are compounds of low polarity (halides, oxides, sulphides, etc.), examples being $SbCl_3-SnCl_4$ and TiO_2-SiO_2.[65]
2. All AX–BY, AX–BX, and AX–AY systems in which one component is a typical salt or a saltlike compound separate only when four different ions are present; when there is a sharp difference in characteristics between the cation pairs and the anion pairs; and when one component is a simple low-polarity compound like a halide or an oxide of a metal having 18 + 1 to 18 + 4 electrons in their outer shells (Ag, Pb, Tl), or even an acid anhydride such as B_2O_3, TiO_2, V_2O_5, etc. If the original components do not conform to these conditions, they may be established by interaction between the components.

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ADVANCES IN THE CHEMISTRY OF BARBITURIC ACIDS

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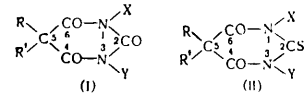
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INTRODUCTION

Barbituric acids (I) and (II) are compounds containing the 2,4,6-trioxohexahydropyrimidine or 2-thio-4,6-dioxohexahydropyrimidine ring; in the latter case they are designated as 2-thiobarbituric or simply as thiobarbituric acids:



(I) (II)

Although one representative of this class of substances — hydurilic acid (5,5'-bisbarbituric) — had been prepared by Schlieper[1] as long ago as 1845, very little was known about the barbituric acids until the beginning of the 20th century, when Fischer and coworkers worked out a convenient method for their synthesis[2] and observed their well-known therapeutic properties[3].

In the course of the last 25 years our knowledge of the barbituric acids has extended remarkably. In addition to their soporific and analgesic properties, barbituric acids possess antiinflammatory[4], antisclerotic[5], and bacteriostatic[6-8] properties; they lower the blood pressure[9-11], they find use in the treatment of sugar diabetes[12] and as antidotes against adder poison[13]. Barbituric, and especially thiobarbituric acids, are used in photography[14-31], as antioxidants[32-34], and as catalysts for the polymerisation of

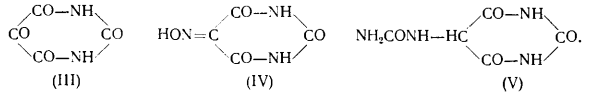
halogenated vinyl monomers[35] and of styrene[36]. Azo-dyes containing the 2,4,6-trioxohexahydropyrimidine nucleus possess a good covering power, and are suitable for the dyeing of wool, silk, and cellulose[37-39].

Barbituric acids are finding more and more applications in analytical chemistry: for the preparation of buffer solutions in the range pH 6–9, where only a few substances are suitable[40], as very sensitive indicators in acidimetric titration[41], as reagents for the determination of small quantities of Ag, Hg, Cu, Pd, Pt, Ir, In, Au[42], and also of chloride and cyanide ions[43]. Barbituric acid (I) (where R = R' = X = Y = = H) condenses with formaldehyde, giving useful resins[44]. The insecticide[45] and herbicide[46] action of barbituric acids may also be mentioned.

Apparently, barbituric acids play a not insignificant part in biological processes. Desoxyribonucleic acids, which are supposed[47] to carry the hereditary factors in chromosomes, contain thymine groups, which gives barbituric acid on biological oxidation[48,49]. The pyrimidine ring enters into the molecule of vitamin B_2 (riboflavine); among the metabolic products of *Lactobacillus casei*, barbituric acid is found after introduction of this vitamin into the nutritional medium[50]. A series of microorganisms assimilate barbituric acid, using the energy of its decomposition to CO_2, NH_3, and malonic acid for their life processes[48,51-53].

Up to the present, nearly 2000 barbituric acids have been synthesised. Some of these are produced on a commercial scale. In the USA the yearly production of barbituric acids amounts to 300–400 tons[54]; in the USSR the production is rapidly growing and the output of barbituric acids in 1955 exceeded that of 1950 by 204%[54].

In a review article we cannot deal with all the details of the chemistry of barbituric acids; in what follows the most important aspects of their synthesis and chemical properties are considered, with a brief mention of all secondary questions and a list of the relevant literature. As a basis, only "typical" barbituric and thiobarbituric acids are taken, in which the substituents in position 5 are linked with the hexahydropyrimidine nucleus by a carbon–carbon bond, while X and Y may be any groups. Such a limitation may be artificial to a certain extent, but at the same time, it is necessary to separate the barbituric acids from derivatives of alloxan (III), and violuric (IV) and pseudouric acids (V):



(III) (IV) (V)

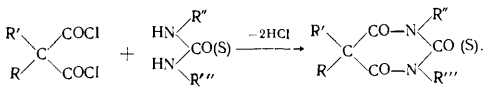
I. ADVANCES IN THE SYNTHESIS OF BARBITURIC AND THIOBARBITURIC ACIDS

From the practical point of view it is important to distinguish between methods applicable in acid (or neutral) and in alkaline media. The first include syntheses of barbituric acids from malonic acids and their acid chlorides and also from alloxan and other heterocyclic compounds related to barbituric acids; the second includes the synthesis of barbituric acids from malonic and cyanoacetic esters, from amides of malonic acids, from lactonic esters, and also from derivatives of urea, cyclised for the most part in the presence of alkaline condensing agents.

A. REACTIONS IN AN ACID OR NEUTRAL MEDIUM

1. Preparation of Barbituric and Thiobarbituric Acids from Malonic Acid Chlorides

One of the oldest methods of preparation of barbituric acids is the reaction of the acid chlorides of substituted malonic acids (malonyl chlorides) with urea* or thiourea[56-73]:



This reaction does not require condensing agents and occurs in neutral solution under relatively gentle conditions (~ 100°, 5–6 h); therefore synthesis of barbituric acids unstable under the conditions of alkaline condensation is possible. Thus, 5,5-diphenylbarbituric acid, which could not be synthesised from 5,5-diphenylmalonic ester[74], has been prepared from the acid chloride of diphenylmalonic acid[75]. The reaction with malonyl chlorides is particularly convenient for the preparation of 1,3-disubstituted barbituric acids[63,76]. *N,N'*-diphenylthiourea in general does not react with malonic esters, while its condensation with the acid chlorides of malonic acids takes place spontaneously[67].

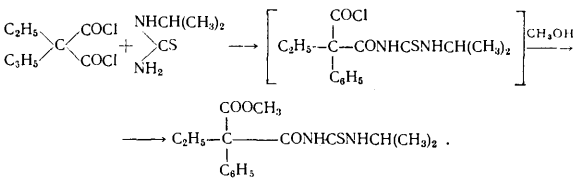
The condensation of the acid chlorides of malonic acids with urea usually occurs with equimolar proportions of the components without a solvent[56,57,62-64,68], or in ether[77], chloroform[65], toluene[58], xylene[62], dioxane[61], or pyridine[70].

In the reaction of thiourea with malonyl chloride many resinous reaction products are formed together with the thiobarbituric acid[60,78].

The principal side reactions in the barbituric acid synthesis are acylation of the barbituric acid already formed and the thermal dissociation of the *N*-substituted urea[67]. The following series of *N*-substituted ureas is arranged in order of increase of thermal instability[79,80]:

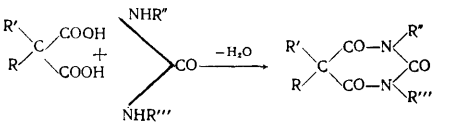
$$CO(NH_2)_2 \leqslant CO(NHCH_2C_6H_5)_2 < CO(NHC_6H_{13})_2 \leqslant CO(NHC_3H_5)_2 = $$
$$= CO[NHCH(CH_3)_2]_2 < CO[NHC(CH_3)_3]_2.$$

According to the observations of Boon and coworkers[78], α-ethyl-α-phenylmalonyl chloride reacts anomalously with *N*-isopropylthiourea, forming (after working up the product with CH_3OH) *N*-(α-methoxycarbonyl-α-phenylbutyryl)-*N'*-isopropylthiourea:



2. Preparation of Barbituric and Thiobarbituric Acids from Malonic Acids

The condensation of malonic acids with urea in the presence of a dehydrating agent,

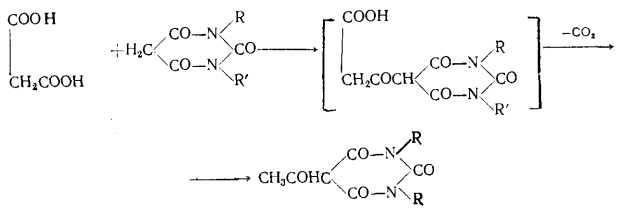


was the first preparative method for the synthesis of barbituric acids[81]. Since then, this reaction has been repeatedly

* Instead of urea 1-cyanoguanidine, NH = $C(NH_2)NHCN$, can be used[55].

used for the synthesis of *N*-substituted barbituric acids[57,67,68,73,76,82-94]. Phosphorus oxychloride[57,76,81,84,85,88,90,92,93], acetic anhydride[68,82,83,86,89,91,94], and acetyl chloride[76,87] have been used as condensing agents. The advantage of the latter two agents is that under the action of the water removed during the condensation, they decompose into acetic acid, easily removable from the reaction medium; however, the possibility of acetylating the already-formed barbituric acids is a serious drawback. None of the condensing media mentioned possesses an obvious advantage[76]. With phosphorus oxychloride, the reaction is carried out in chloroform; the acetic anhydride and acetyl chloride themselves serve as solvents, or the reaction is carried out in glacial acetic acid; the temperature varies between 50° and 100°.

The sphere of application and effectiveness of the methods of preparing barbituric acids from malonic acids and from malonyl chlorides are approximately the same. However, the significantly smaller thermal stability of the malonic acids[95], in comparison with their esters or acid chlorides, gives rise to a variety of side reactions, which much reduces the value of the method, making it impossible to synthesise a number of barbituric acids in this way (e.g. 5-halogeno or 5-alkenyl derivatives). The important side reaction is the acylation of the barbituric acid already formed by a second molecule of malonic acid[57,67,85,92]. A part of the malonic acid is also expended on the acylation of the second component of the reaction — urea or its derivatives[57]:

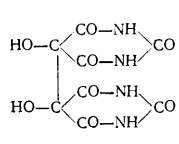


On increasing the scale, the quantity of acylated side products increases disproportionately quickly[57], which lowers the yields of barbituric acids in large batches; in order to suppress this side reaction, it is necessary to avoid excess of urea[91] and prolonged heating of the reaction mixture[92]. The formation of malonuric acids[89] and their amides[94] as by-products has also been noted.

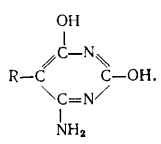
Attempts to avoid the difficulties due to the instability of the malonic acids by replacing the latter by cyanoacetic acid[56], and also by the use of 1-cyanoguanidine[55] were unsuccessful.

3. Preparation of Barbituric Acids from Other Nitrogenous Heterocyclic Compounds

The initial heterocyclic compounds for the synthesis of barbituric acids are most often alloxan, alloxantin (VI), and derivatives of aminouracil (VII):



(VI)



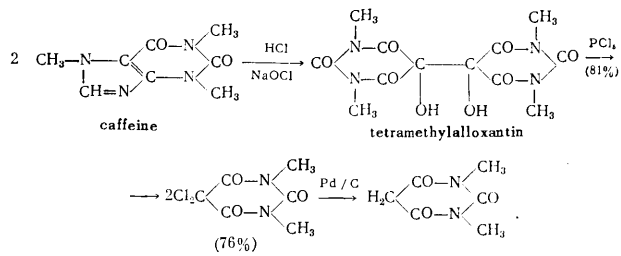
(VII)

Alloxan condenses with compounds containing an active methylene group in the presence of 20% oleum, acetic anhydride, or concentrated hydrochloric acid, to form 5-alkylidenebarbituric acids or 5-substituted-5-hydroxybarbituric acids which are later transformed into 5-mono-substituted barbituric acids[62,96-99].

In the reaction of alloxan with benzene in the presence of sulphuric acid 5,5-diphenylbarbituric acid is formed with a five-membered oxide as a by-product[62,98,99].

A series of syntheses of barbituric acids from their 5,5-dihalogeno-, 5-hydroxy-, 5-nitroso-, and other derivatives has been described, starting usually with alloxan[77,100-103].

Alloxantin was already used at the time of Bayer[104] for the preparation of *N*-substituted barbituric acids, which are formed by heating alloxantin with concentrated sulphuric acid. A very economical synthesis of 1,3-dimethylbarbituric acid from tetramethylalloxantin (prepared from caffeine) has been described[86]:



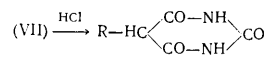
caffeine

tetramethylalloxantin

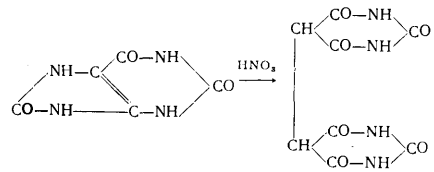
(76%)

In the preparation of 1,3-dimethylbarbituric acid from malonic ester and dimethylurea the yield does not exceed 37%.

It is easy to prepare barbituric acids from aminouracil (VII)[105-107]:



Uric acid can be converted into 5,5'-bisbarbituric acid[1,108]:



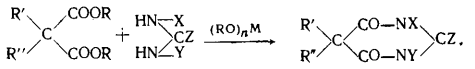
Other examples of the preparation of barbituric and thiobarbituric acids[67,109] from related heterocyclic compounds have been described.

B. REACTIONS IN AN ALKALINE MEDIUM

4. Preparation of Barbituric and Thiobarbituric Acids from Malonic Esters

At the present time the most commonly used method of preparation of barbituric and thiobarbituric acids is the condensation of malonic esters with urea, thiourea, guanidine, or their derivatives, in an alcoholic medium in

the presence of alcoholates of alkali- or alkaline-earth metals:



where Z = 0.5 or NH*; n = 1 or 2.

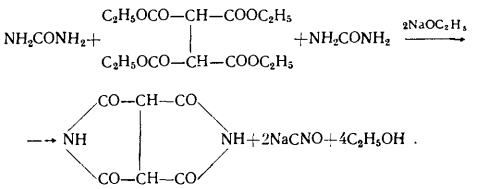
The majority of known barbituric and thiobarbituric acids have been synthesised by this method[11,30,37,55,62,68,73,74,78,105,108,110-263].

The merits of the method described are its universality, the relative accessibility of the original malonic esters, the high yields (70–98%) of barbituric acids, and their purity, which is particularly important in pharmacological investigations[200].

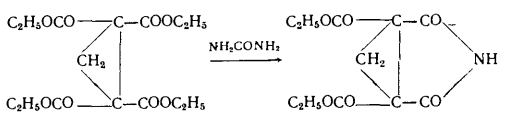
At the same time, the method has definite limitations. The malonic esters containing, for example, 1-alkenyl[110,149], cyclopropyl[264-268], β-hydroxyalkyl[242], or heterocyclic[121,146,162,267] radicals, and also substituted malonic esters with a keto group in the β-position[268-270], are not stable in an alkaline medium. However, for this group of esters the suggestion of Jacobson[271] that the monosodio derivative of urea, $NH_2C[ONa]=NH$, be used as second component may prove fruitful, because the monosodio derivative reacts with malonic esters in the absence of a condensing agent at room temperature giving barbituric acids in a yield of ~80%.

Arylalkyl-, diaryl-, and t-alkylbarbituric acids cannot be conveniently prepared from the corresponding malonic esters on account of the difficulty of obtaining these, and the low yields of the barbituric acids[62,151,228,272,273]. It was not possible to synthesise 5,5-diphenyl-[74], 5-p-nitrophenyl-[274], 1-methyl-5-isopropyl-5-β-diethoxyphosphoryloxyethyl-[11], 5-propyl-5-α-ethoxyvinyl-[110], and 5-ethyl-5-α-butoxyvinylbarbituric[110] acids in this way. Bisalkylmalonic esters, $(C_2H_5OCO)_2CRCR(COOC_2H_5)_2$, and also certain alkylidenemalonic esters, do not react with urea in the presence of sodium ethylate[275]. It is also impossible to prepare 1,3-dialyl- and 1,3-diarylbarbituric acids by the condensation of malonic esters with substituted ureas[275,276].

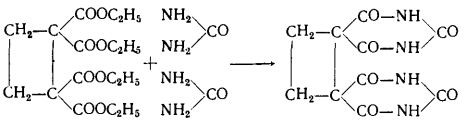
Unexpectedly, ethanetetracarboxylates and urea do not form bisbarbituric acid, but ethanetetracarboxydiimide[252]:



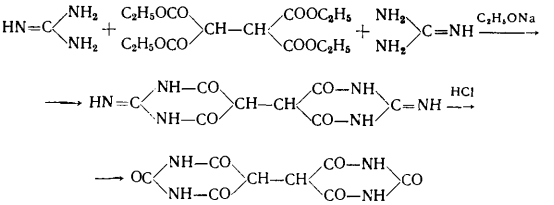
The reaction between cyclopropanetetracarboxylates and urea proceeds analogously[277]:



It should be noted that the cyclobutanetetracarboxylates under the same conditions give the "normal" product of the reaction, cyclobutanebisspirobarbituric acid[277]:

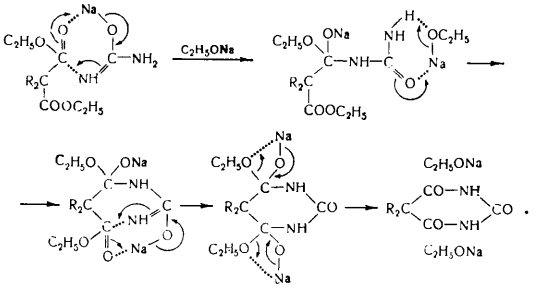


Ethanetetracarboxylates react normally with guanidine hydrochloride forming diiminohydurilic acid, which on boiling with hydrochloric acid is transformed to hydurilic acid[108]:



The mechanism of the condensation of malonic esters with urea in the presence of sodium ethylate has not been investigated in detail. It is quite probable that, as suggested by Skinner and coworkers[278], the reaction proceeds via the formation of the sodio derivative of urea.

Considering, according to the theory of Nesmeyanov and coworkers[279,280], the possibility that the process proceeds with the transfer of the reaction centre, one can regard the condensation mechanism as a threefold "diene" synthesis with the participation of σ,π-conjugated bonds:

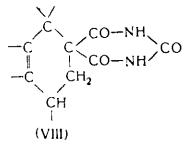


The great facilitation of the reaction on replacing the urea by guanidine, thiourea[278], or monosodiourea[271] favours such a scheme, as does also the need for an excess of alcoholate to obtain maximum yields of the barbituric acids[281].

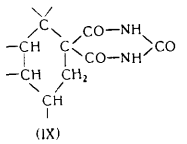
The structure of both components exerts an enormous influence on the course of the reaction and the yield of barbituric acids. As a rule[117,118], monosubstituted malonic esters condense more easily with urea than do the disubstituted derivatives; with increase of branching of the substituent, particularly at the α-carbon atom, the reactivity of the malonic esters is reduced[118,166]. This explains the difficulty

* When Z = NH, the product of the reaction is transformed to barbituric acid by hydrolysis with hydrochloric acid.

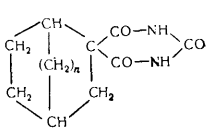
encountered by Levina and coworkers[128,170,172,180,277,282] in the synthesis of "spiro"-barbituric acids of types (VIII), (IX), and (X):



(VIII)



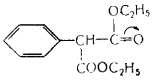
(IX)



(X)

n = 1 or 2

A phenyl group at the α-carbon atom of the malonic ester[98,283] powerfully inhibits the condensation; this is evidently connected with a reduction of the electron density on the O atom in the system (cf. the above scheme of condensation):

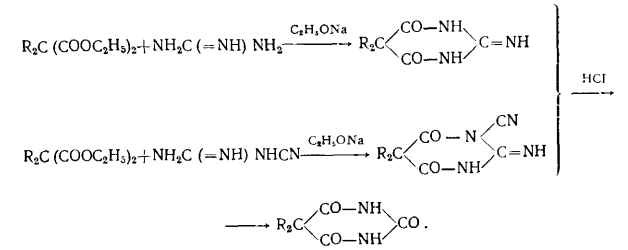


Electron-donating *ortho*- or *para*-substituents in the benzene ring considerably weaken its inhibiting action[74]. The inhibiting influence of the naphthyl radical is weaker in comparison with the phenyl[204]. Electron-acceptor substituents (such as the NO_2 group, for example) in the α-position to the ethoxycarbonyl group of the malonic ester makes the condensation more difficult[147,148,152,201]. Difficulty has also been encountered in the preparation of 5-trimethylsilylmethyl-[171] and 5-alkylsulphonylmethylbarbituric acids[207] from the corresponding malonic esters:

$(CH_3)SiCH_2CH(COOC_2H_5)_2$; $RSO_2CH_2CH(COOC_2H_5)_2$.

In place of the ethyl esters of malonic acids, the butyl[167,200] or methyl esters can enter into the reaction[62]. Sodiomalonic ester has also been used[140].

As second component of the condensation, urea, guanidine[112,155,167,187,191,238,244,261,263,284], and 1-cyanoguanidine[55,202,285] are employed. The use of the last two reagents leads to the formation of products requiring additional working up for transformation to barbituric acids:



The length of the carbon-carbon chain of the substituents of the N-alkylureas does not influence the course of the reaction[125]. N-Phenylurea condenses with malonic esters more easily than N-alkylurea[281]; symmetrical N,N'-diarylureas do not form barbituric acids with disubstituted malonic esters[2,86], while with monoalkylmalonic esters the reaction goes easily and the yields of barbituric acids exceed 60%[86].

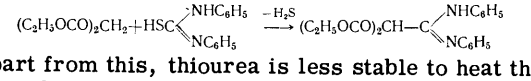
The best condensing agent is sodium ethylate[82,130,281,286-288], but CH_3ONa[62,78,82,139,141,162,167], iso-C_3H_7ONa[114], C_4H_9ONa[138,145,227], $C_5H_{11}ONa$[289], $(CH_3O)_2Mg$[111,122,124,130,153,177,190,286], caustic alkalis, $NaNH_2$, Na-cyanamide[290], and $CaCl_2$[226,290] have also been used. Most commonly, the condensation in the presence of sodium ethylate is carried out in absolute ethyl alcohol. Reactions in toluene[129] or without solvent[163,193] have also been described. Constancy of temperature during the reaction ensures constancy of yields[286].

The condensation of malonic esters with urea is often complicated by side reactions. Among the products formed in this way the following have been separated: esters of carbonic acid[115,194], esters and amides of monocarboxylic acids, esters of carbamic acid*, and esters of malonamic acids[74,76,113,115,162,194,291].

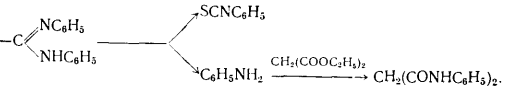
The very reactive 5-monoalkylbarbituric acids are oxidised by atmospheric oxygen to 5-hydroxy-5-alkylbarbituric acids[293-295].

Malonic esters react more easily with thiourea than with urea[140,278], and form 2-thiobarbituric acids. However, the yields are, as a rule, lower than those of the corresponding O-analogues, which is explained by the greater complexity of the reaction.

In view of the relatively great tendency to thiol formation[296], thiourea may react in the thiol form with the CH_2 group of the malonic ester[276]:



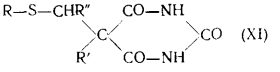
Apart from this, thiourea is less stable to heat than urea, and one of the products of its thermal decomposition may in its turn condense with the malonic ester[276]:



With a large excess of thiourea, the malonic ester may condense with two of its molecules[291]; for example:

$$R_2C(COOC_2H_5)_2 + 2NH_2CSNHCH_2CH = CH_2 \rightarrow$$
$$\rightarrow R_2C(CONHCSNHCH_2CH = CH_2)_2 + 2C_2H_5OH.$$

Comparison of a series of results from the literature shows that in the preparation of thiobarbituric acids by this method the behaviour of the reaction system is often the reverse of that observed for barbituric acids. While branched malonic esters give better yields of barbituric acids when sodium butylate is used, than with sodium ethylate, the reverse is generally true in the condensation with thiourea[166]. In the synthesis of barbituric acids of structure (XI),



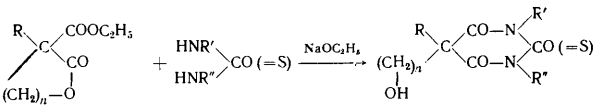
(XI)

an excess of sodium ethylate usually favours the condensation[118], but thiobarbituric acids of the same type can be prepared only with an equivalent quantity of sodium ethylate[117,118]. The condensation of malonic esters with urea in the presence of $(CH_3O)_2Mg$ gives barbituric acid in a 96% yield; the analogous synthesis with thiourea leads to the formation of only an insignificant yield of thiobarbituric acid[298]. In the synthesis of barbituric acids an excess of alcohol is immaterial, but the yield of thiobarbituric acid is sharply lowered thereby[297]. The best condensing agent for the synthesis of thiobarbituric acid is apparently lithium ethylate[297].

* Esters of carbamic acid may be formed during the alcoholysis of urea[292].

5. Preparation of Barbituric and Thiobarbituric Acids from Lactonic Esters

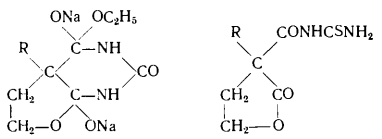
The particular method of the synthesis of barbituric acids from lactonic esters,



is directly related to the possibility of preparing barbituric acids from malonic esters, as lactonic esters are easily prepared from the latter, but differs in its gentler reaction conditions. The advantages of this method are clearly shown in the case where the reactants are unstable to heat, particularly in the presence of alkali, e.g. the preparation of 5-(β-hydroxyethyl)- and, in particular, of 5-(2-hydroxyprop-2-enyl)barbituric acid[299]*.

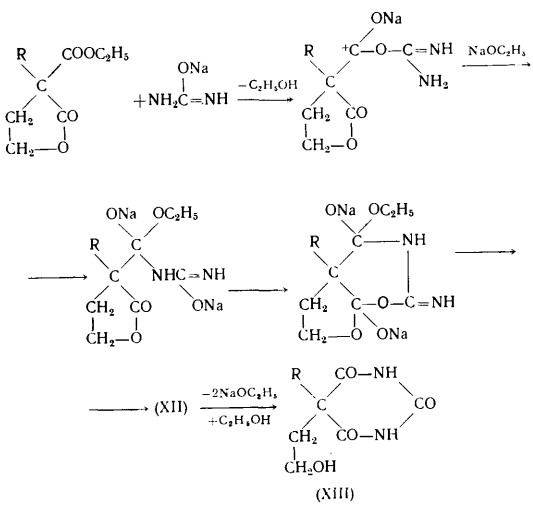
The application of the method has been limited, because, up to the present, only γ-lactonic esters have been used[112, 146,148,165,278,299-303]. Also, according to the investigations of van Zyl and van Tamelen[303], monosubstituted barbituric acids cannot be prepared by the condensation of the corresponding lactonic esters with urea.

The following intermediates have been isolated[278,302]:



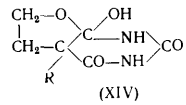
(XII)

on the basis of which Skinner and coworkers[278] have suggested the following scheme for this reaction:



(XIII)

The product of the reaction can have the β-hydroxyethyl (XIII) or the hemiacetal (XIV) structure,

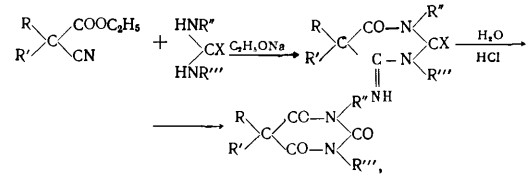


(XIV)

the consequence of which is that there is a certain dualism in the chemical behaviour of barbituric acids of this kind[148]. As alcohols they form chloroalkylbarbituric acids with fuming hydrochloric acid; at the same time, alkaline hydrolysis does not give a trace of unsaturated acids.

6. Preparation of Barbituric and Thiobarbituric Acids from Cyanoacetic Esters

By the interaction of cyanoacetic esters with urea (or guanidine) in the presence of an alkaline condensing agent, an iminobarbituric (or diiminobarbituric) acid is first formed, and subsequently hydrolysed to barbituric acid by mineral acids:



where X = O or = NH.

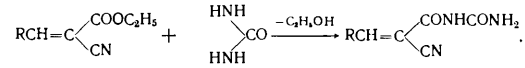
In the USSR this method is used for the commercial synthesis of hexenal (sodium salt of 5-cyclohexenyl-3,5-dimethylbarbituric acid)[304].

Having much in common with the syntheses of barbituric acids from malonic esters (for example identical conditions of reaction, the same condensing agents), this method possesses the defect of involving two stages, although the loss of product at the stage of the hydrolysis of the imino-acid is usually not great*.

The yields of barbituric acids synthesised by this method[132,137,169,178,263,304-321], are lower in the majority of cases, than by synthesis from malonic esters[137,311].

However, inhibition due to steric hindrance is not so strong in the case of cyanoacetic esters as in condensations with malonic esters, and this explains the advantages of this method for the preparation of barbituric acids with α-branched substituents[306], spirobarbituric[175], and 5-substituted 5-phenylbarbituric acids[307].

Alkylidene- or arylidenecyanoacetic esters do not form the corresponding iminobarbituric acids[315]; the reaction stops at the stage of the alkylidenecyanoacetyl urea:



It was not possible to prepare 5-(4-thiazolyl)barbituric acid by this method in consequence of resinification of the reaction mixture[315].

* The reference (299) is incorrect (Ed. of Translation).

* The hydrolysis of 2-thioiminobarbituric acids is accompanied by the formation of the corresponding barbituric acids[175,318].

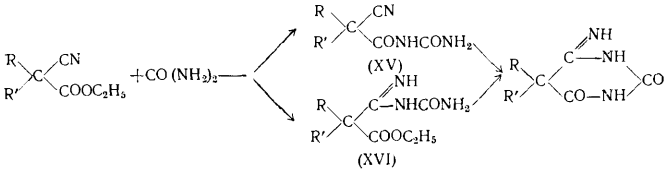
As the synthesis of barbituric acids from cyanoacetic esters is a two-stage reaction, the use of guanidine instead of urea [242,263,305,310,312,313,315,318] is completely justified in all cases, since the number of stages is not increased, and the duration of the reaction is diminished [305,322]. Instead of urea 1-cyanoguanidine [313] can also be used.

In the reaction mixture the cyanoacetic esters also undergo some alcoholysis involving splitting off the ethoxycarbonyl group and the formation of the nitrile, the yield of which may amount to 60% [305,311]:

$$R_2C(CN)COOC_2H_5 + C_2H_5OH \xrightarrow{NaOC_2H_5} R_2CHCN + CO(OC_2H_5)_2.$$

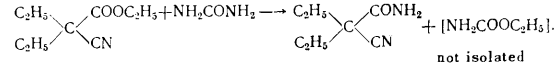
The replacement of sodium ethylate by isopropylate, and of urea by guanidine, diminishes the extent of alcoholysis [305].

In Lund's opinion [315] the formation of iminobarbituric acids from cyanoacetic esters proceeds in two ways:



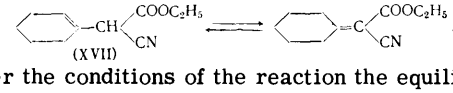
As the cyclisation of compound (XVI) occurs very easily, it is not possible to detect it in the reaction mixture; the cyclisation of compound (XV) occurs with difficulty. Thus, the results of the condensation depend on the rates of formation of (XV) and (XVI), in view of which the ratio of the iminobarbituric acid and cyanoacetyl urea (XV) remains almost constant on carrying out the reaction under various conditions. Cyanoacetyl urea has been repeatedly found among the products of the reaction [318,321].

Conrad and Zart [319] separated diethylcyanoacetamide from the reaction mixture in the preparation of 5,5-diethylbarbituric acid from diethylcyanoacetic ester and urea:



Lund [315] noticed an interesting complication in a reaction involving cyanoacetic esters with a double bond in the β-position to the CN group: α-(cyclohex-1-enyl)cyanoacetic ester (XVII) does not form iminobarbituric acid, decomposing only to α-(cyclohex-1-enyl)cyanoacetylurea, while the α-ethyl derivative (XVIII) condenses with urea to 5-ethyl-5-(cyclohex-1-enyl)-4-iminobarbituric acid.

The reason for such a difference in the behaviour of substances (XVII) and (XVIII) consists, according to the author, in the presence of tautomers in the first of them:



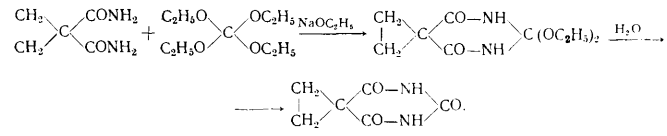
(XVII)

Under the conditions of the reaction the equilibrium is almost wholly driven to the side of the alkylidene derivative incapable of cyclisation with urea (cf. p. 442). Such an isomerisation is impossible for (XVIII) and the reaction proceeds normally.

7. Preparation of Barbituric Acids from Amides of Malonic Acids

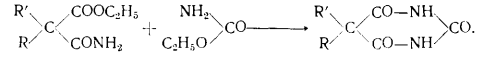
The possibility of preparing barbituric acids from amides of malonic acids bridges the gap to syntheses carried out in an acid medium, since this reaction can occur not only in alkaline, but also in neutral and even in an acid medium, according to the stability of the second component.

The condensation of malonic diamides with orthocarbonates takes place in the presence of sodium ethylate without heating [323], for example:



Diphenyl carbonate forms diethylbarbituric acid with diethylmalonic diamide only on heating for 18 h at 200°–280° [324]. 5-Phenyl- and 5,5-diphenylbarbituric acids were prepared by heating the corresponding malonic diamides with oxalyl chloride in benzene without a condensing agent [62,162]. A series of barbituric acids have been synthesised by the condensation of malonic diamides with phosgene (in toluene, 150°) [62,187].

Tanaka and Sugawa [325] found that the esters of carbamic acid condense with esters of malonamic acids in the presence of isopropylate, cyclohexylate or sodium amide to the corresponding barbituric acids:

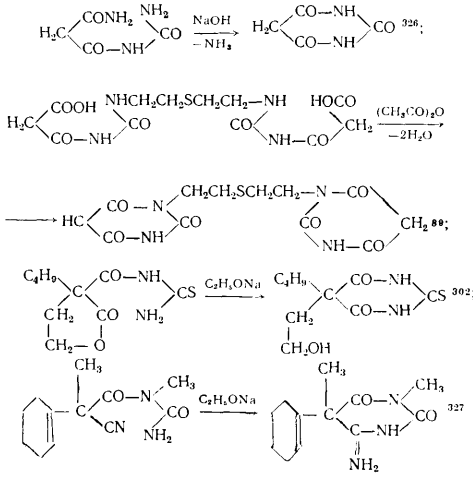


Malonamic esters condense in the presence of sodium ethylate with urea, forming barbituric acids [319].

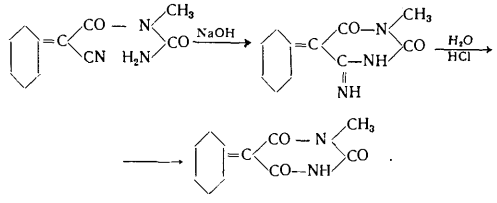
Esters [94] and ureides [70] of malonuric acids have also been used for the preparation of barbituric acids, without much success.

8. Preparation of Barbituric and Thiobarbituric Acids by Cyclisation of *N*-Substituted Ureas

The cyclisation of derivatives of urea to barbituric and thiobarbituric acids has no value for synthesis, but it indirectly indicates the possibility of *N*-derivatives of urea capable of cyclisation to barbituric acids being intermediates in the above reactions. For example:



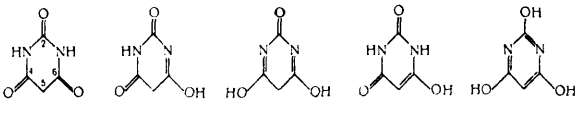
Nakamura[328] synthesised 1-methyl-5-cyclohexylidene-barbituric acid in 90% yield by heating cyclohexylidene cyanoacetylmethylurea with 10% caustic soda and subsequent acid hydrolysis of the reaction product:



This fact clearly contradicts Lund's view that alkylidene-cyanoacetic esters are not capable of forming barbituric acids with urea[315]. By an analogous method Nakamura prepared some 5-Δ^1-cyclohexenylbarbituric acids[328].

II. REACTIVITY OF BARBITURIC AND THIO-BARBITURIC ACIDS

The hexahydropyrimidine nucleus of barbituric acid, which contains three carbonyl groups and four mobile hydrogen atoms, possesses a high degree of reactivity. The variety of possible chemical transformations of barbituric acids is further increased because trioxohexahydropyrimidines are capable of a multiplicity of enolic forms. To date, derivatives of the following forms of barbituric acid have been described:



The possibility of the formation of the conjugated-bond systems,

$$\overset{\frown}{CH}=C^{+}-\overset{\frown}{O}^{-} \text{ and } \overset{\frown}{O}=C-\overset{\frown}{N}-H$$

determines the power of trioxohexahydropyrimidines to react at different active centres; for example, alkylation occurs under some conditions at the nitrogen, and under other conditions at carbon atom 5.

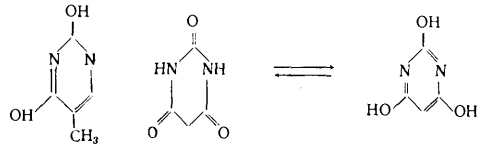
As it possesses two mobile atoms of hydrogen in position 5, barbituric acid may enter into almost all the reactions characteristic of malonic esters. In addition to this, the carbonyl group is capable of being reduced, of condensing with compounds containing mobile hydrogen atoms, and of exchanging its oxygen for halogen atoms.

Thiobarbituric acids are even more reactive, as the sulphur in position 2 may become quadrivalent and the C=S bond is relatively easily reduced.

1. Tautomerism

In the light of all that has been said above, the question of the possibility, the nature and the direction of tautomeric transformations in the series of barbituric acids is highly significant. Unfortunately, in spite of the large number of investigations in this field[19,57,75,79,85,251,293,294,329,337], the problem has not received a final solution.

The spectra show that barbituric acids enolise in solutions. Heyroth and Loofbourow[331], comparing the ultraviolet spectra of different pyrimidines, discovered that as the number of double bonds increases the absorption maxima shift to the long-wave part of the spectrum. Noticing the proximity of λ_{max} for barbituric acids and thymine,

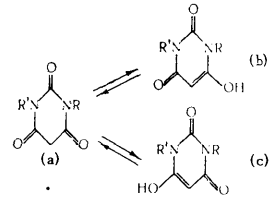


thymine barbituric acid

the authors suggested that the trienol tautomer of barbituric acids exist, but only in a strongly alkaline medium[338]. The existence of the trienol form, however, became doubtful when it was established[329], in 1952, that barbituric acid has a spectrum similar to that of 1-methylbarbituric acid, in which the trienol form is impossible. Even earlier[251,336], the analogy in the spectra of barbituric, 5-methylbarbituric, and 1,5-dimethylbarbituric acids was noted. In addition, in view of its aromatic structure, the trienol form should give a considerably lower extinction coefficient than is actually observed[329].

Erlenmeyer and coworkers[339] showed that in heavy water all four hydrogen atoms of barbituric acid are replaced by deuterium. From this it follows that the enolisation can proceed at least in one pair of neighbouring atoms, for example, in the following positions: 1, 2; 1, 6; and 5, 6; or 2, 3; 3, 4; and 4, 5.

The majority of investigators[57,251,329,336,340] consider that mono- and disubstituted barbituric acids in aqueous solutions undergo only single enolisation; for example, for 1,3-disubstituted barbituric acid the forms (a), (b), and (c) are possible:



Form (a) should be stable in acid, and forms (b) and (c) in alkaline solutions (pH = 7–11)[57,329]. With a rise of alkalinity of the medium, the degree of enolisation increases, as shown by the increase of u.v. absorption[57,251,333].

Sheinker and Pomerantsev[341] have demonstrated that barbituric acid is trioxohexahydropyrimidine in the crystalline state; in its infra-red spectrum there are intense bands corresponding to the CO groups and no absorption band is observed, which could be related to C=C or C=N linkages.

Interesting data on the barbituric acid tautomerism in solution may be gained from the investigation of their acid properties. In view of the high ionisation constant of barbituric acid in comparison with those of 5,5-dialkylbarbituric acids, Wood and Anderson[94] concluded that unsubstituted barbituric acid exists in solution in the enol form. However, alkylation of the sodium salts of barbituric acids yields *C*- or *N*- derivatives, not those of the enol form.

According to the observations of Biggs[334], 5,5-diethyl--1,3-dimethylbarbituric acid cannot enolise, neither does it exhibit acid properties. Its alcoholic solutions do not possess a band in the region of 241 mμ, where less substituted barbituric acids possess more or less intense absorption

bands. 5-Cyclohexenyl-1,5-dimethylbarbituric acid, in which enolisation is possible only in the 2,3- or 3,4-positions, shows weak acidity. If neither nitrogen atom carries substituents, the enolisation being thereby appreciably facilitated, the acidity is strongly increased. Barbituric, 1-methylbarbituric, and 1,3-dimethylbarbituric acids have close pK values, apparently because the enolisation in the 2,3- and 3,4-positions in the first two is weak.

The chemical transformations of barbituric acids are complicated, as it is necessary to assume the existence of all the forms described above in equilibrium with one another. Apparently, such difficulties can be overcome by considering charge displacement.

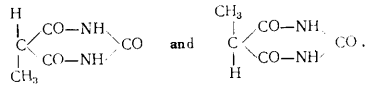
$$H-\overset{\frown}{N}-C=\overset{\frown}{O}^{(-)} \text{ or } H-\overset{\frown}{CH}-C=\overset{\frown}{O}^{(-)},$$

in the ring of the barbituric acids under the influence of various factors (medium, irradiation, chemical reagents). The trioxohexahydropyrimidine system is strongly polarisable, and such electron displacements may be accomplished in it with relative ease.

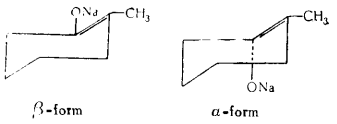
Thus, derivatives of numerous "tautomers" can be formed in the reaction, as a consequence of the distribution of electron density in the pyrimidine ring* characteristic of each case [75,92,105,133,293,332,335,342-344].

The spectra of the barbituric acids apparently reflect differences of the degree of polarisability of the trioxohexahydropyrimidine system dependent on the nature and distribution of substituents in the nucleus.

In the series of 5-monosubstituted barbituric acids stereoisomerism is possible as a consequence of the hindrance to the rotation of the ring by heteroatoms**:



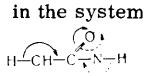
Nishikawa [294] succeeded in separating α- and β-forms of the sodium salts of these acids, differing in solubility and pH of their solutions**:



β-form α-form

On heating, the α-form is transformed into the β-form. Stereoisomerism may also arise due to asymmetric centres in the side chains of barbituric acids [63,345]. In the case of tetraalkylbarbituric acids, the separation of such stereoisomers into their enantiomorphs is extraordinarily difficult, because they are neutral substances and do not give salts with optically active bases or acids [63].

* This distribution may be anticipated from a knowledge of the electron structure of the reactants and the influence of the medium. In particular, in the system

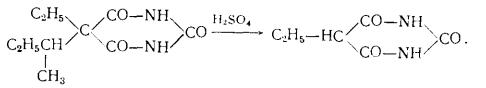


the electron displacement in the direction of the continuous arrows is preferred to that of the dotted arrows.

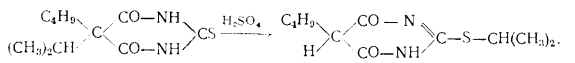
** These statements follow the abstract quoted [294]; they would not now be considered valid (Ed. of Translation).

2. General Stability of the 2,4,6-Trioxohexahydropyrimidine Nucleus

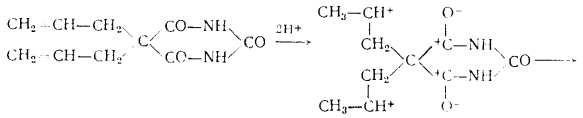
The 2,4,6-trioxohexahydropyrimidine nucleus is, in general, fairly stable to the action of various chemical reagents. It is not affected by such reducing agents as $SnCl_2/HCl$ [101,346-348] and zinc-dust in CH_3COOH [349] or water [350], or on hydrogenation in the presence of PtO_2 [37,274]. The aromatic nuclei of phenylbarbituric acids can be nitrated [37,274,351-353] and sulphonated [352] under the usual conditions without disruption of the pyrimidine ring. The pyrimidine nucleus of barbituric acids containing an amino group in the substituent chain is not ruptured during diazotisation and coupling [37,274,278,347,353]. Cold concentrated H_2SO_4, as a rule, does not split the nucleus of barbiturates [208,354,355]; however, in the case of 5,5-dialkylbarbituric acids containing a secondary alkyl, the latter is split off by the action of H_2SO_4 [355,356]:



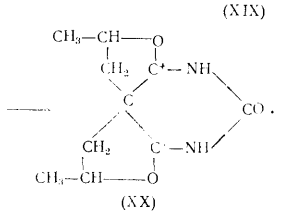
Monoalkylbarbituric acids, even those containing a secondary alkyl, are not changed by the action of H_2SO_4 [355]. Under analogous conditions, thiobarbituric acids isomerise into S-alkylated reaction products [357]:



Allyl groups in position 5 diminish the stability of the trioxohexahydropyrimidine nucleus, evidently on account of the possible formation of the unstable carbonium ion (XIX), later cyclising to (XX) [355]:

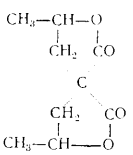


(XIX)



(XX)

The ion (XX) becomes later stabilised in one way or another. Actually, 5,5-diallylbarbituric acid is easily transformed by concentrated H_2SO_4 into the lactone



Apparently the same substance was obtained by Leuchs and Lemcke [358] by the action of fuming HBr on diallylbarbituric acid.

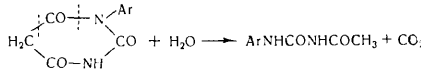
Spirobarbituric acids can also be split by the action of HBr [150]. The nucleus of 5,5-dialkylbarbituric acids is not split on boiling with concentrated HBr, and only sometimes is a secondary alkyl removed, as by the action of H_2SO_4 [152,355]. On heating barbituric acid with concentrated HCl to 200°, the pyrimidine ring is broken down, malonic acid, urea, ammonia, acetic acid, and CO_2 being formed [109].

Aluminium chloride, like sulphuric acid, removes alkyl groups from barbituric acids; but it does not form *S*-alkyl derivatives from thiobarbituric acids[355].

Fialkov and Rapaport[359] remark that the nuclei of 5,5 diallylbarbituric and 5-s-pentyl-5-β-bromoallylbarbituric acids are not decomposed by a solution of ICl in HCl, even at 70°–80°.

Chromic acid (at ~20°)[360], $K_2Cr_2O_7$ in H_2SO_4[350,361], and 30% H_2O_2 do not disrupt the nucleus of barbituric acid in the cold.

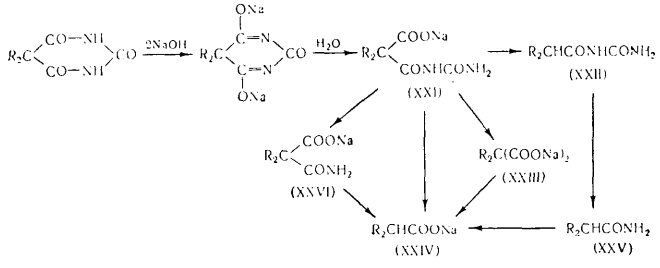
Usually, barbituric acids are stable to water — they are decomposed by it only on many hours' boiling at 5–10 atm[362]; however, *N*-arylbarbituric acids, according to Ridi's observations[84], are broken down as follows on boiling in water:



Spirobarbituric acids, on prolonged heating with water, decompose with separation of ammonia[323] and formation of the corresponding malonic acids[145]. Tetrasubstituted barbituric acids are still less stable[363].

In contrast to the barbituric acids, their sodium and potassium salts (and consequently the barbituric acids themselves in the presence of alkali) are extremely unstable, particularly in aqueous or alcoholic solution. As the instability of the sodium salts of barbituric acids in aqueous solutions has great significance in medical practice, considerable attention has been devoted to the hydrolysis of these salts[84,98,202,229,234,238,254,281,283,284,323,362,364-373].

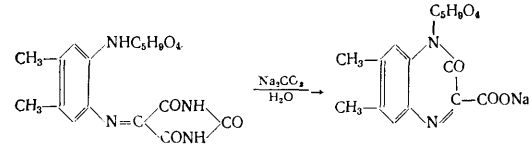
The literature gives information on the formation of the following products of barbituric acid hydrolysis: (XXI)[202,229,238,283,362,372]; (XXII)[202,229,354,362,365]; (XXIII)[84,202,234,283,284,323,367,373]; (XXIV)[98,284,365,367-369]; (XXV)[362,368]; (XXVI)[369].



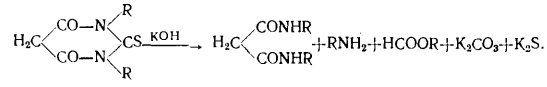
The scheme indicates the possibility of the formation of at least six substances according to the conditions of hydrolysis. Compounds of type (XXI) are products of the hydrolysis of the sodium salts of barbituric acids at ordinary temperatures; sometimes, however, (XXI) may not be formed, because the relatively most stable 5,5-dialkylbarbituric acids are not decomposed by cold alkali. In the case of the most unstable barbituric acids (those with unsaturated and *N*-aryl groups, and spirobarbituric acids) hydrolysis in the cold leads to (XXII), (XXIII), and even to (XXV); in the majority of cases, for the formation of these hydrolysis products, boiling the barbituric acids (or their sodium salts) with 10–20% NaOH is required. The compounds (XXVI) and (XXIV) are formed only on boiling the reaction mixture. The sodium salt of a substituted acetic acid (XXIV), urea, ammonia, carbon dioxide, $NaHCO_3$, and Na_2CO_3 are the final products of the hydrolysis of barbituric acids. In separate experiments, the decomposition of (XXI) to (XXII), (XXIII), and (XXIV), of (XXII) to (XXIV), and of (XXVI) to (XXIV) has been demonstrated.

Addition of alcohol or glycerol to solutions of sodium barbiturates decreases the rate of their hydrolysis[254].

The sodium salt of a substituted malonamic acid (XXVI) is formed in the hydrolysis of 1-(*N*-barbiturylidene)-4,5-dimethyl-2-D-ribitylaminoaniline* by boiling with 27% Na_2CO_3:[371]



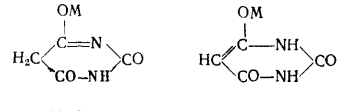
The action of KOH on *N*,*N*-disubstituted thiobarbituric acids splits the pyrimidine ring[364]:



The 2,4,6-trioxohexahydropyrimidine ring is also destroyed by caustic alkalis without a solvent. Molle and Kleinst[374], by slow fusion of 5,5-diethylbarbituric acid with NaOH, obtained the sodium salt of diethylacetic acid and ammonia. Later Jorissen[326] discovered cyanoacetic acid among the products of this reaction.

3. Reactions of Barbituric Acids Involving the Mobile Hydrogen Atoms

(a) Acid properties. Barbituric and thiobarbituric acids, by the action of hydroxides or salts, can exchange one or two atoms of hydrogen for a metal, forming salts of the types (XXVII) and (XXVIII), apparently according to whether the metal–oxygen[94,279] bond is strongly or weakly ionised:



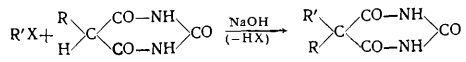
With the silver ion, a salt is formed (XXVIII) that gives on subsequent alkylation, C_5-derivatives[92,342]; alkali metals form salts of the type (XXVII), capable of being alkylated not only at the N atom, but also at the C_5 atom. If two substituents are present in position 5, only the form (XXVII) is possible.

Salts of alkali metals[370,375-377], Al[378,379], Ca[380], Ba[373], Ag[373,381,382], Hg[383-386], Cu[373,387-389], Co[379,390,391], Ni, Mn, Fe, Mg[379], and Pb[373] have been described. The salts of Co, Ni, and Cu have a complex composition and have been little investigated. Barbituric acids form stable salts with organic bases[392]. The imide hydrogen of barbituric acids reacts with organomagnesium compounds[393].

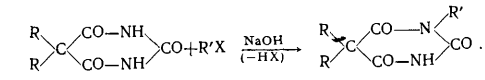
In these reactions, the trioxohexahydropyrimidines behave as typical acids. However, with strong mineral acids barbituric acids also behave as bases; in particular, they are readily titrated with perchloric acid[394].

* D-Ribityl = D-ribose residue – $CH_2CHOHCHOHCHOHCH_2OH$ (– $C_5H_{11}O_4$).

(b) *C*- and -alkylation (arylation). Alkyl (aryl) derivatives of barbituric acids may arise by substitution on carbon 5 or on the nitrogen; the hydrogen on the nitrogen is replaced with more difficulty than on carbon 5, and accordingly, when a choice is possible, it is the latter, and not the imide hydrogen, that is replaced in the first instance[337,395-398]:



or



These reactions are widely utilised for the synthesis of 5-substituted and *N*-substituted barbituric acids (particularly for those that cannot stand vigorous conditions of synthesis), because the process occurs under gentle conditions, and gives good yields of the desired reaction product. Thus, this reaction is convenient for the introduction of unsaturated radicals into the nucleus of barbituric acid (cf. Table).

TABLE. Comparison of various methods of synthesis of barbituric acids (according to Goldhahn and Barth[368]).

5,5-Substituents in the synthesised barbituric acid	Yield of acid, %	
	from malonic esters	by the introduction of unsoturoted radical into the 5-monosubstituted barbituric acids
Allyl, allyl	37	84
Crotyl, crotyl	75	97.5
Ethyl, crotyl	50	97
Ethyl, allyl	50	65
Allyl, crotyl	49	68

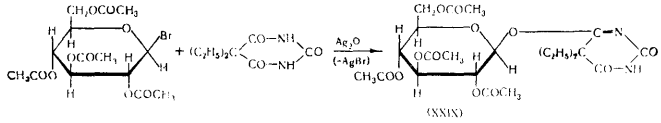
By this method, it is possible to synthesise barbituric acids that are impossible to prepare from malonic esters, in view of the instability of the latter. In particular, 5-acetanilidobarbituric acids were thus prepared[399]. From the corresponding malonic ester, 1,3,5-trimethyl-5-β--diethylaminoethylbarbituric acid could not be prepared; but it is easily synthesised by the interaction of 1,3,5-trimethylbarbituric acid with $ClCH_2CH_2N(C_2H_5)_2$.[363]

A second advantage of this method is the high purity of the product obtained. This is particularly important in the synthesis of low-melting *N*-substituted barbituric acids, which in the presence of impurities separate in the form of non-crystallising syrups[400].

In some cases, however, the reaction is complicated. In the alkylation of 5-isopropylbarbituric acid by α,α-dimethylallyl bromide in the cold, the yield of 5-isopropyl--5-(3-methylbut-2-enyl)barbituric acid is 27% (on heating even less), whereas this acid is prepared from malonic esters in a yield of 67%[193].

The preparation of *C*-alkylbarbituric acids by the interaction of monoalkylbarbituric acids with α-$C_{10}H_7CH_2Br$[203] was not successful. Even such an active agent as allyl bromide does not form a 5-allyl-derivative with 1-ethoxycarbonylmethyl-5-acetylbarbituric acid[57]. It was not possible to prepare 5-phenyl-5-cyclohexylbarbituric acid by the interaction of cyclohexyl bromide with 5-phenylbarbituric acid[62] or 5-methyl-5-cyclooctylbarbituric acid from 5-cyclooctylbarbituric acid and methyl iodide[184].

In view of the ability of barbituric acids to enolise, a competing formation of *O*- and *N*-derivatives might have been expected on straight alkylation of the sodium salts of 5,5-dialkylbarbituric acids. However, until very recently, no indisputable examples of *O*-alkylation were known; the claim of Marotta and Rosanova[330] to have prepared *O*-derivatives by the methylation of 5,5-diethylbarbituric acid by diazomethane was proved erroneous[63]. However, in 1953 Snyder and Link[109] succeeded in preparing *O*-derivatives (XXIX) by the interaction of tetraacetyl-D-glucosylbromide with 5,5-diethylbarbituric acid in the presence of an excess of Ag_2O and of quinoline:

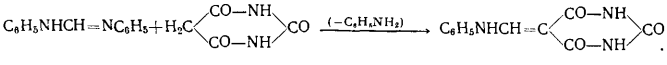


(XXIX)

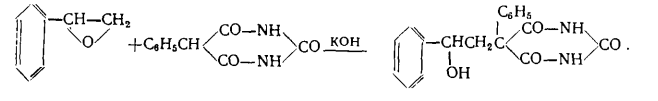
A synthesis of (XXIX) directly from the silver salt of 5,5-diethylbarbituric acid did not succeed.

Most frequently, alkylation* has been used for the preparation of 5-substituted barbituric acids.

Alkyl[87,153,284,290,400-402] and alkenyl[6,57,62,161,184,193,200,257,290,368,403-409] iodides and bromides, halogenoarylmethanes[60,86,203], halogenopyridines[367,410,411], α-halogenoketones[369,399,412-414], *N*-chloro-*N*-acylanilines[415], and various α-halogenomethyl derivatives of heterocyclic compounds[24,130,159,416] have been used as *C*-alkylating agents. Alkylation by alkyl halides is difficult[153,402]. Instead of alkyl halides, alkyl *p*-toluene sulphonates[417] can be utilised. Formamidines[60] also react at the C atom:



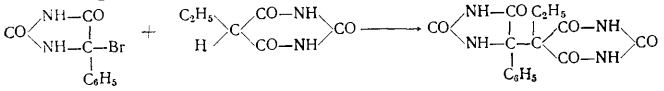
By interaction with the alkali-metal salts of 5-monobarbituric acids, epoxides give small yields of 5,5-disubstituted barbituric acids[303], containing an alcohol group in the substituent:



Thiobarbituric acids polymerise under these conditions[418]. *C*-alkylated barbituric acids may arise in the presence or absence of strong alkali; in the latter case alkylating agents containing mobile halogen atoms are used, for example, allyl halides[6,57,290,404], bromophenylhydantoin[419], α-$C_{10}H_7CH_2Br$[203], $C_6H_5COCH_2Br$[412], *p*-$C_2H_5OC_6H_4NCl$. .$COCH_3$[415], $ClCH_2COCH_3$[399], and $ClCH_2CONHC_6H_5$[399].

* Barbituric acid is easily acylated in the 5-position by acid anhydrides and chlorides[91,364]. Urea forms with barbituric acid a 5-NH_2CO-derivative[364].

The reaction is carried out in an aqueous-alcoholic medium by heating in the presence of an equimolar quantity of sodium acetate. The addition of potassium or sodium iodide considerably accelerates the reaction and raises the yield of *C*-alkylated barbituric acid[399,415]. Phenylbromohydantoin, possessing an extremely active bromine atom, reacts with barbituric acids even in the cold and in acetic acid, forming 5-alkyl-5-phenylhydantoinylbarbituric acids, for example:



In most cases, *C*-alkylation is carried out in aqueous alcohol in the presence of $N-3N$ NaOH, since in this case it is easily reproducible and gives high yields of *C*-alkylated barbituric acids[57,193,202,233,250,254,369,398,405,413,416,417,420,421]. Even here the addition of iodides facilitates the yield of the desired product[233,257] (for example, in the synthesis of 5-acetonylbarbituric acids, the yield is raised from 10 to 75%[413]). Apparently, the influence of the NaI added in the alkylation of barbituric acids (or bromides) involves the conversion of the chlorides by sodium iodide into alkyl iodides which react much more easily with the barbituric acids[233]. The addition of Cu powder[416] or $CuSO_4$[57,369,405,408] also acts favourably. The reaction proceeds also in the absence of alcohol, but usually more slowly[254]; the yields of substituted barbituric acids reach 90%[202]. 5-Triphenylmethylbarbituric acid was prepared by fusing $(C_6H_5)_3CCl$ with barbituric acid in vacuo[284]. The preparation of tri- and tetraalkylated acids by direct alkylation of barbituric acid has, up to the present, not been successful[337], but tetra-*p*-nitrobenzylbarbituric acid was prepared[395] by the reaction of barbituric acid with an excess of *p*-nitrobenzylchloride.

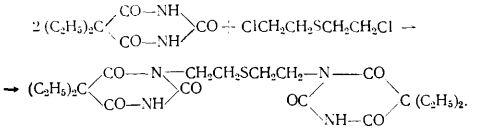
Among the side reactions we should mention *N*-alkylation in those cases where it is possible[63,396-398], and dehydrohalogenation when polyhalogeno compounds[401] (for example, 1,2,3-tribromopropane) or compounds with a mobile halogen atom (triphenylchloromethane)[250] are used on alkylating agents.

2-Thiobarbituric acids, in particular 5-alkyl-substituted compounds, are capable of alkylation on the sulphur atom[408,422-424].

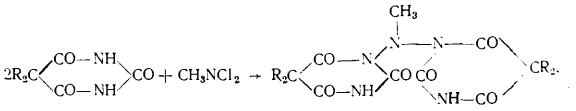
A comparison of the influence of alkylation conditions on the yield of barbituric acids is given by Gabel'[290] and Halpern and coworkers[425].

N-Alkylation of 5,5-disubstituted barbituric acids proceeds under the same conditions and with the same catalysts as does *C*-alkylation[9,57,62,193,284,285,319,354,370,425-449]. Among *N*-alkylating agents, *p*-nitrobenzyl bromide and phenacyl bromide are relatively important, because these *N*-derivatives of barbituric acids crystallise well, have definite melting points, and serve for the identification of barbituric acids[435,442,444,445,449,450]. A microchemical modification of the reaction has been described by Reimers[443].

It is interesting that solutions of veronal inactivate mustard gas, forming a non-poisonous compound with it[447]:



Dichloromethylamine forms with 5,5-dialkylbarbituric acids the very unstable methylaminobisbarbituric acid[446]:



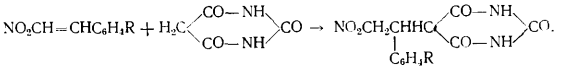
Cases of intramolecular *N*-alkylation have been described[451].

It is possible to alkylate 2-iminobarbituric acids (primary products of the interaction of malonic ester with guanidine) or 4-iminobarbituric acids (prepared from cyanoacetic ester and urea). The products can easily be converted into barbituric acids[261,285,319].

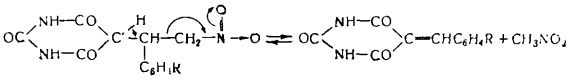
Some reagents usually react with the 1,3 hydrogen atoms. These include compounds of the type RHgX[386,452], phenylmercury hydroxide[453], dimethyl sulphate in alkaline solution[101,127,345,454-457], diethyl sulphate[345,456], diazomethane, and diazoethane[62,63,350,456,458]. Biltz and Wittek[91] introduced a single methyl group into position 5 of 1,3-dimethylbarbituric acid with the help of a large excess of diazomethane, but they did not succeed in substituting the second H atom in position 5 by a CH_3 group in the same way. The hydrogen atoms on both nitrogen atoms seemed to be quite equivalent in chemical reactions[63,91].

Not all derivatives of barbituric acid are equally easily methylated; thus, hydurilic acid is not methylated by dimethyl sulphate[100]. *N*-Allyl derivatives of thiobarbituric acid cannot be synthesised by the reaction of allyl bromide with the sodium salt of thiobarbituric acid in aqueous or alcoholic solution; ring rupture occurs with the formation of 2-propenethiol[370].

(c) Substitution by addition. Barbituric acid and its 5-monoalkyl derivatives enter into a series of reactions involving addition[459,460]. Compounds with conjugated double bonds combine with barbituric acid without any catalyst[459]:



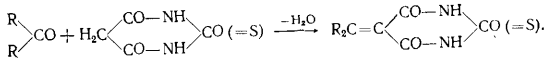
The velocity of the reaction depends on the concentration of barbituric acid. Reduction of the electron density on the carbon atom which is attacked by the anion of the barbituric acid increases the speed of the reaction. Increase of the dielectric constant of the reaction medium has the same effect[461]. The final products of the reaction are unstable and rapidly decompose on storage[459]:



Attempts to use in this reaction $C_6H_5C \equiv CCH_2OH$[462], $CH_2=CHPO(OR)_2$[11], cinnamic and acrylic acids, methyl acrylate and benzalmalonic ester were unsuccessful.

(d) Condensation reactions. A considerable number of communications[60,66,76,82,88,199,241,344,349,364,421,463-489] have been published about investigations of the condensation of barbituric and thiobarbituric acids and their

1,3-disubstituted derivatives, with aldehydes and ketones:

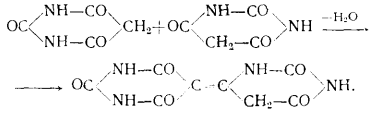


The ketones react with appreciably greater difficulty than the aldehydes; this is the basis of a method of separating them by boiling their mixtures with an aqueous solution of barbituric acid[223,464].

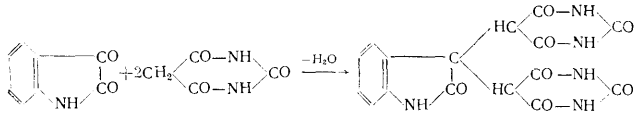
The reaction is carried out by boiling an equimolar mixture of the reagents in alcohol[82,344,421,481,482], water[199,344,349,469,483], pyridine[375,482,486], glycerol[373], or glacial acetic acid[467,488]. Sparingly soluble, sometimes coloured, compounds are thereby produced: in consequence, this reaction has been frequently suggested for the identification and quantitative estimation of aldehydes[76,384,463,490-492] and barbituric acids[379].

Aliphatic aldehydes form compounds without sharp melting points and often of a resinous nature, but the reaction goes smoothly with aromatic and heterocyclic aldehydes, and the condensation product separates quantitatively[464]. Substitution on the nitrogen does not influence the rate of the reaction[66,76]. In a number of cases the reaction is accelerated by the addition of bases: trimethylamine[486], hydrazine hydrate[484], piperidine[480].

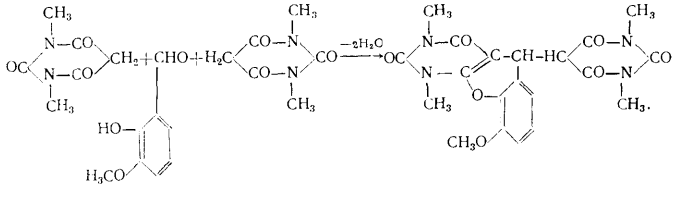
A second molecule of barbituric acid may act as carbonyl component[373]:



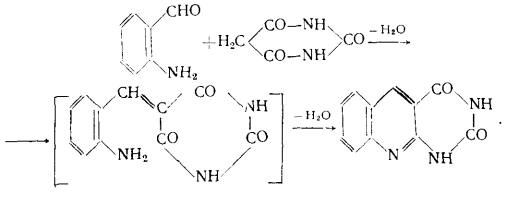
Some limitations and complications in the reaction of aldehydes and ketones with barbituric acids are known, particularly in the case of ketones. Thus, in an alkaline medium barbituric acid does not condense with isatin; in an acid medium bisbarbituric acids are formed[472]:



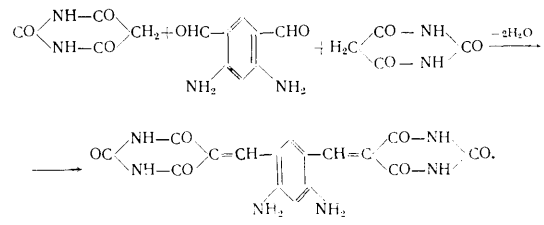
An analogous reaction is given by salicylic aldehyde[349,464]. Orthovanillin forms with 1,3-dimethylbarbituric acid *o*-vanillylidenebisdimethylbarbituric anhydride[464]:



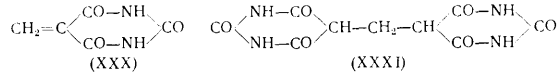
By the condensation of *o*-aminobenzaldehyde[349], and also of 2-amino-4-nitrobenzaldehyde[344] with barbituric acid, a diazoacridine ring is formed:



When 4,6-diaminoisophthalic aldehyde is used, the reaction follows the normal path[482]:

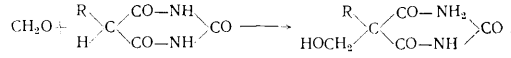


It is impossible to prepare methylenebarbituric acid (XXX)[464] from formaldehyde and barbituric acid; however, its ammonium salt was synthesised by the reaction of barbituric acid and urotropine[474]; on neutralisation of this salt by hydrochloric acid, methylenebisbarbituric acid (XXXI) was obtained instead of (XXX).

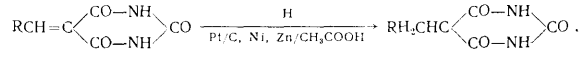


(XXX) (XXXI)

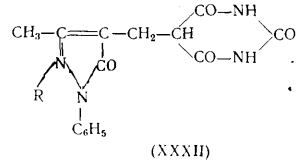
Formaldehyde condenses with 5-substituted barbituric acids forming methylol derivatives[493]:



The condensation of barbituric acids with aldehydes may be important for the preparation of 5-monosubstituted barbituric acids, which are easily formed in quantitative yield by the catalytic hydrogenation or reduction by zinc and acetic acid of arylidene- or alkylidenebarbituric acids:



In this, in spite of the additional stage in the reaction, the yields of 5-substituted barbituric acids are usually higher than in their syntheses from malonic esters[199]. With some types of barbituric acids, e.g. (XXXII), this reaction is the only means of preparation, since the corresponding malonic and cyanoacetic acids and esters cannot stand the conditions of the condensation:

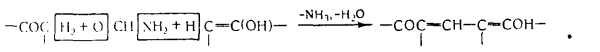


(XXXII)

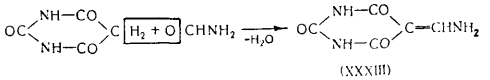
The synthesis of 5-monoalkylbarbituric acids from aliphatic carbonyl compounds may be achieved, even in a one-stage hydrogenation of a mixture of aldehydes and barbituric acids in the presence of palladium in an alcoholic solution[494,495]. The aldehydes react more rapidly than the ketones, and among the ketones the low-molecular more rapidly than the high-molecular. Cyclic ketones are more active in this reaction than aliphatic ketones with the same number of carbon atoms; unsaturated carbonyl compounds react more rapidly than the saturated analogues.

Formamide and its *N*-derivatives[364,470,474,487] condense with barbituric acids in the same way as aldehydes. It is

interesting that at the same time formamide reacts with $-CH_2CO-$ groups in the usual way, dimerising them into oxonols:

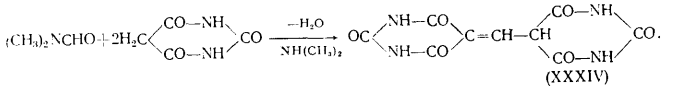


For barbituric and thiobarbituric acids the basic reaction is the formation of aminomethylene compounds (XXXIII), evidently as a result of the high mobility of the hydrogen in the methylene groups[475]:



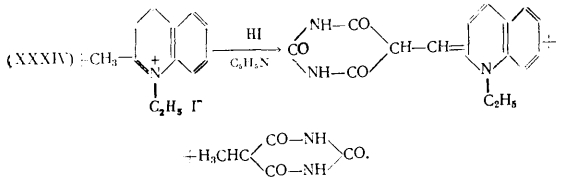
(XXXIII)

Oxonols of type (XXXIV) (see below) are formed in insignificant quantities in this way. In the preparation of (XXXIII) instead of formamide, ammonium formate[470] can be used and even formic acid itself[237]; the reaction of barbituric acid with *N*-formylaniline proceeds in this way[467]. However, if in place of formamide, dimethylformamide is used, the normal product of the reaction, methylidynebisbarbituric acid[475] (XXXIV), is almost exclusively formed:



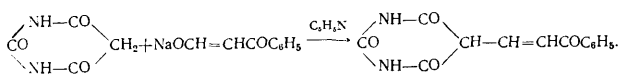
(XXXIV)

Oxonols of type (XXXIV) can react with compounds possessing an active CH_3 group to form merocyanines, for example[496]:



The merocyanines of barbituric and thiobarbituric acids may also be prepared by another method[497-504]; they find application as sensitisers for photographic emulsions[496-506].

The reactions of barbituric acids with $C_6H_5COCH = CHONa$[505] proceed analogously, for example:

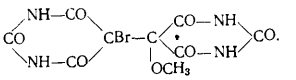


(e) Halogenation. The trioxohexahydropyrimidine nucleus is easily halogenated. By passing chlorine into an aqueous suspension of barbituric acid[85,91] or its 5-alkyl derivatives[103] at 30°–40°, or into an alcoholic solution of barbituric acid at 0°[100], 5,5-dichlorobarbituric and 5-alkyl-5-chlorobarbituric acids, respectively, are formed in good yield.

Sulphuryl chloride (SO_2Cl_2) in chloroform acts similarly to chlorine[103]. The chlorination of barbituric acids with potassium perchlorate in hydrochloric acid has been described[90,100]. By the action of calcium hypochlorite in acetic acid on 5,5-diethylbarbituric acid, 1,3-dichloro-5,5-diethylbarbituric acid is formed[507]; this is a good chlorinating agent for unsaturated compounds.

The bromination of barbituric acids proceeds just as easily, leading to 5-bromo-[81,508] and 5,5-dibromobarbituric acids[85,90-92,509,510], tribromoacetureides[508] being formed as side products.

Hydurilic acid, on bromination in the presence of methanol, decomposes into the compounds[101,346]



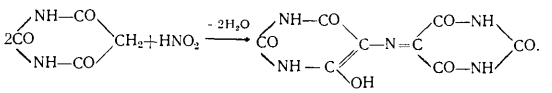
By the action of iodine chloride on 5-alkylbarbituric acids, Fresenius[511] prepared 5-iodo-5-alkylbarbituric acids; 5-hydroxy- and 5-chlorobarbituric acids were also formed.

(f) Oxidation. Various products are obtained by the oxidation of barbituric acids. Chromic acid oxidises barbituric acid to alloxan, and a mixture of $NaClO_3 + V_2O_5 + H_2SO_4$[512] acts in the same way. Alloxan is also formed on the oxidation of alkylidene- or arylidenebarbituric acids[483]. Nitric acid reacts vigorously with monoalkylbarbituric acids, forming numerous products, including alloxan[90].

5-Mono-substituted barbituric acids are easily oxidised to the corresponding dialuric (5-hydroxybarbituric) acids, even by atmospheric oxygen[294,295,513]. $K_2Cr_2O_7$ in water or glacial acetic acid[123,514] and H_2O_2 and Na_2O_2[123,513,515] act similarly.

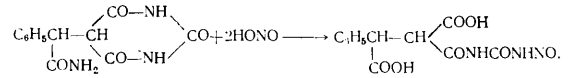
5,5-Dialkylbarbituric acids are much more stable to oxidation than monoalkylbarbituric acids[293].

(g) Other reactions involving the mobile hydrogen atoms. Barbituric and thiobarbituric acids and also their monoalkyl derivatives are very easily attacked by HNO_2, yielding violuric acid[87,90-92,516-518]. From barbituric acid, purpuric acid is formed as a by-product:

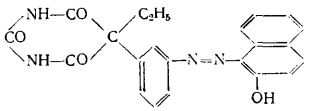


By reacting thiobarbituric acid with ethyl nitrite in alcohol, the analogous thiopurpuric acid is obtained as the chief product of the reaction[519].

Diazotisation of α-(5-barbituryl)phenylacetamide by sodium nitrite at -5° leads, unexpectedly, to the breakdown of the ring[234]:



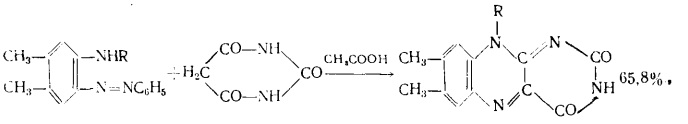
The nucleus of 5,5-disubstituted barbituric acids is usually not affected on diazotisation; thus, from 5-(*m*-aminophenyl)-5-ethylbarbituric acid a diazonium salt was obtained, which gave the azo-dye (XXXV)[351] with β-naphthol:



(XXXV)

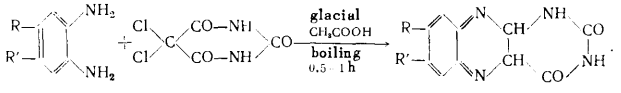
By reaction with nitrogen-containing compounds, barbituric acids form a series of technically valuable substances. Thus, p-$(CH_3)_2NSO_2C_6H_4NHSO_2C_6H_4NH_2$-$p$, after diazotisation, reacts with barbituric acid forming an orange azo-dye [520].

Tischler and coworkers [521], starting from barbituric acid, accomplished a direct synthesis of riboflavine (vitamin B_2):

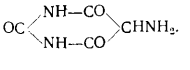


where R = D-ribityl (cf. p. 446).

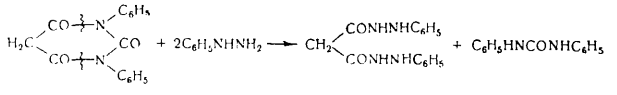
Alloxazines, related to riboflavine, are also formed in the reaction of substituted o-phenylenediamines with 5,5-dichlorobarbituric acids [522], for example



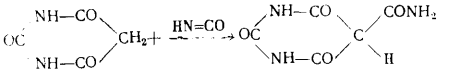
By boiling with phenylhydrazine in water, in acetic acid, or without a solvent, barbituric acid gives uramil [523,524]:



N-substituted barbituric acids, under these circumstances, react with rupture of the ring [524]:



Isocyanic acid reacts with barbituric acid to give malobiuric acid [525]*:



The interaction of barbituric acid with mercury fulminate, $Hg(CNO)_2$, in a KCN solution leads also to the formation of malobiuric acid [474].

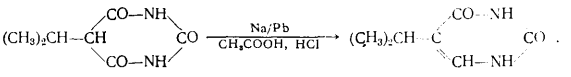
4. Reactions of Barbituric and Thiobarbituric Acids Involving the Carbonyl (Thiocarbonyl) Groups

The reactivity of the carbonyl group of barbituric acids depends to a considerable extent on the nature of the substituents in the 5-position.

On electrolytic reduction of barbituric acid, the reaction stops at the stage of formation of hydrouracil or trimethyleneurea [526]; hexahydropyrimidine is not obtained in this way.

The 5-monoalkylbarbituric acids are reduced similarly, but with much more difficulty. The introduction of two alkyls in position 5 changes the behaviour of the acid: as a consequence of the small tendency to enolisation in the 5,5-dialkyl barbituric acid, only the urea-type carbonyl group is reduced, and not the malonic ester residue [78,526,527].

5-Isopropyluracil is obtained from 5-isopropylbarbituric acid by the action of a sodium–lead alloy (30% Na) in a mixture of hydrochloric and acetic acids:

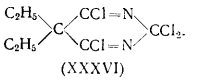


Lithium tetrahydroaluminate reduced 5,5-disubstituted barbituric acids only to the corresponding trimethyleneurea [528].

It should be mentioned that, in comparison with CO groups in a carbon chain, the 4,6-carbonyl groups in barbituric acid possess a somewhat lowered activity as a consequence of the mutual influence of the CO and NH groups. They are not reduced by the action of Raney nickel or sodium amalgam in HCl [78]; 4-chloroquinaldine, which usually reacts with $-CH_2-CO-$ groups, does not enter into reaction with barbituric acids [529].

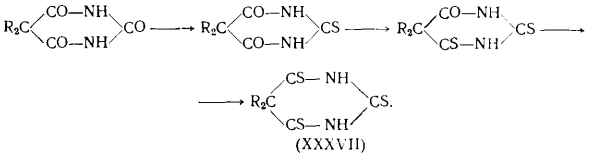
On boiling with $POCl_3$, monoalkylbarbituric acids react in the trioxopyrimidine form [244,293], forming 2,4,6-trichloropyrimidines; in the presence of $C_6H_5N(CH_3)_2$, 4,6-dichloro-2-(*N*-methylanilino)pyrimidine [530,531] is formed as a side product.

By the action of PCl_5 on 5,5-diethylbarbituric acid, a tetrachloro derivative (XXXVI) is obtained in small yield with a considerable quantity of diethylcyanoacetyl chloride [293,343]:



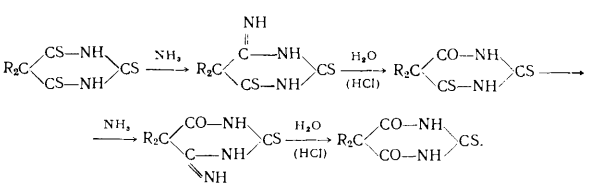
(XXXVI)

Heating barbituric acids with phosphorus trisulphide in tetralin at 225° leads to the formation of trithiobarbituric acids of the type (XXXVII) [532,533]. When phosphorus pentasulphide is used, 2-thiobarbituric and 2,4-dithiobarbituric acids can be isolated from the reaction mixture, in addition to trithiobarbituric acids; the replacement of oxygen by sulphur evidently occurs in stages [532]:



(XXXVII)

By the subsequent action of ammonia and hydrochloric acid, it is easy to prepare monothiobarbituric acids from di- and trithio-derivatives [532]:

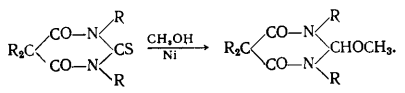


The CS group of 2-thiobarbituric acids is considerably more reactive than the carbonyl group of the barbituric

* At this point the original contains an error, which has been amended in accordance with Curtius' paper [525] (Ed. of Translation).

acids. While sodium amalgam in water hardly acts on veronal, and on prolonged contact, splits it into diethylmalonic acid and urea, 5,5-diethyl-2-thiobarbituric acid is easily reduced in the cold by sodium amalgam to 2-desoxyveronal[70]; the reduction proceeds similarly in the presence of Raney nickel[78,534-536].

On boiling with Raney nickel in methanol, thiobarbituric acids give 2-methoxyhexahydropyrimidine-4,6-diones[537]



2-Phenylimino- and 2-phenylhydrazinobarbituric acids are formed by the action of aniline or phenylhydrazine on thiobarbituric acids[70].

Thiobarbituric acids are easily transformed to barbituric acids by oxidising agents. This reaction can be accomplished with the help of H_2O_2 or $KMnO_4$ in an alkaline medium[484], SeO_2 in acetic acid[538], ICl[539] in hydrochloric acid, sulphuric acid[252,540], nitric acid[318], and by other means[418,541].

III. DETECTION, IDENTIFICATION, AND DETERMINATION OF BARBITURIC ACIDS*

Various colour reactions have been suggested for the detection of barbituric acids. Cobalt salts[542-546] give coloured precipitates or coloured solutions, which may be utilised for the colorimetric determination of barbituric acids.

Barbituric acids form coloured solutions with benzoquinone[547], resorcinol[548,549], H_2SeO_3[379,556], aminoantipyrine in the presence of $K_3Fe(CN)_6$[551], vanillin[548], *m*-nitrobenzaldehyde[552], Fehling's solution[553], formaldehyde, salicylaldehyde[379], and aniline[76].

Many barbituric acids can be identified by microscopic examination of the crystals[554]. However, in view of the wide occurrence of polymorphism among the barbituric acids[57,156,408,435,443,555-559], it is better to use the microscopic method on their compounds with benzylthiourea[560], xanthydrol[57,543,561-565], pyridine[566], urotropine[567], pyrazolones[568,569], ethylenediamine in the presence of $CuSO_4$[571], or with salts of mercury[384,561,565], silver[381], yttrium[572], iron[573], or copper[573].

It is also possible to identify barbituric acids by the different rates of precipitation of dialkylacetylurea ($R_2CHCONHCONH_2$) on heating them to 150° with 0.1 *N* NaOH in sealed capillaries[574].

Mixtures of barbituric acids can be separated by chromatography[545,565,575,576] and electrophoresis[577].

For the quantitative estimation of barbituric acids, acidimetric[578], argentometric[579,580], bromometric[57,578], mercurimetric[581], spectrophotometric[87,582-586], potentiometric[581] and polarographic[587,588] methods have been worked out.

* Methods of determination of barbituric acids are considered in detail in the review of Stainier et al. [570].

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BORAZOLE AND ITS DERIVATIVES

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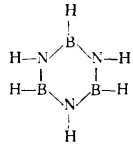
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INTRODUCTION

Borazole is a six-membered heterocyclic compound with alternating BH and NH groups. It is very similar in structure and physical properties to benzene, and is therefore graphically described as "inorganic benzene":



This interesting compound, first obtained in 1926, has attracted the attention of numerous investigators. After a comparatively short period, methods of synthesis of borazole and its various derivatives were discovered, and their physical and chemical properties were quite widely studied. The chemistry of borazole has made particular progress during recent years.

Borazole compounds are interesting, not only theoretically, but also from a practical point of view. Thanks to the comparative stability of the borazole ring to oxidising and hydrolysing agents, various borazole derivatives, such as the hydroxy and amino derivatives, and especially those containing unsaturated hydrocarbon groups, can be used for the synthesis of boron-containing polymers possessing resistance to oils and high thermal stability. Borazole derivatives are also of interest as fuel for rocket motors.

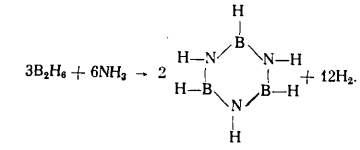
Achievements in the field of the chemistry of borazole were reviewed by Wiberg in 1948[1]. Several problems of the chemistry of borazole were dealt with by Schlesinger and Burg[2], Bauer[3], Stone[4], Zhigach and Kochneva[5], and Mikhailov[6], in reviews on the hydrides of boron, their nitrogen derivatives, and organic compounds of boron. The present paper is a complete review of the literature on borazole which has appeared up to 1958 and, in part, in 1959. All existing methods for synthesising borazole and its derivatives are reported and their value for preparative purposes is assessed.

The synthetic methods are divided into two groups. The first group comprises methods of forming the borazole ring, and the second includes methods based on reactions of functional derivatives of borazole. The second section also includes an account of the most important properties of borazole compounds, enabling valuable interconversions between certain borazole derivatives and others to be accomplished methodically. The general chemical characteristics of borazole compounds are given at the end of the paper.

I. METHODS OF SYNTHESIS OF BORAZOLE AND ITS DERIVATIVES

1. Synthesis from Diborane and its Alkyl Derivatives

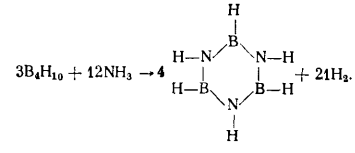
Stock and Pohland[7], in 1926, found that on heating a mixture of diborane and ammonia, or the addition compound $B_2H_6.2NH_3$, at 180°–190° in a sealed tube borazole in 33% yield was formed:



The structure of borazole as a plane six-membered ring with symmetry D_{3h} was established by electron diffraction[8,9].

Subsequently Schlesinger et al.[10] somewhat increased the yield of borazole (to 41%) in this method by raising the temperature to 200°. The reaction is complicated by the formation of a solid polymeric product $(BNH_n)_x$, the elementary composition of which varies with the experimental conditions[11].

Borazole is formed in the same yield by the action of ammonia on tetraborane[12]:

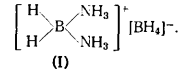


It is obtained also by the action of ammonia on B_5H_{11}.[7]

The mechanism of the formation of borazole from diborane and ammonia still remains obscure. It is suggested that at a high temperature an addition compound of borine and ammonia $BH_3.NH_3$ is formed, which then loses a molecule of hydrogen and is converted into aminoborine $BH_2–NH_2$, the latter by eliminating two hydrogen atoms forming BH=NH, which polymerises to borazole. The general scheme for the formation of borazole proposed by Wiberg and Bolz[11] is represented as follows:

$$3B_2H_6 + 6NH_3 \rightarrow 6H_3B \cdot NH_3 \xrightarrow{-3H_2} 6H_2B{-}NH_2 \xrightarrow{-3H_2} 6HB{=}NH \rightarrow 2B_3N_3H_6.$$

None of the stages has any experimental proof, and the scheme is purely speculative. It is now known that the primary product of the interaction of diborane and ammonia, "diborane diammoniate", $B_2H_6.2NH_3$, is not a dimer of $BH_3.NH_3$[14] but has the structure (I)[16–19]. It is difficult to explain how thermal decomposition of the complex compound (I) can produce a moderate yield of borazole.



(I)

N-Alkylated derivatives of borazole can be obtained starting from diborane. Schlesinger et al.[10] found that *N*-trimethylborazole is formed on heating a mixture of diborane and methylamine, the yield reaching 90% when the components are heated at 180°–200° for 2 h. If, however, a mixture of diborane, ammonia, and methylamine is heated, borazole and its *N*-methylated derivatives are obtained in proportions depending on those of the original reactants[10]: the main product is *N*-methylborazole when equimolar proportions of ammonia and methylamine are taken.

The process can be represented by the general equation

$$3B_2H_6 + 2x\,CH_3NH_2 + 2(3-x)\,NH_3 = 2B_3N_3H_{6-x}(CH_3)_x + 12H_2.$$

Alkyldiboranes also react with ammonia and amines at 190°–200°. Ammonia reacts with methyldiborane[21] or dimethyldiborane[21,22] to form small amounts of borazole, *B*-methyl-, *B*-dimethyl-, and *B*-trimethylborazoles, and also dimethylaminoborine, $(CH_3)_2NBH_2$.

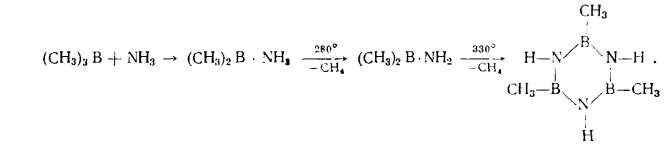
The preparation of borazole and its alkyl derivatives from diborane is very laborious and is of no practical value.

2. Synthesis from Boron Trialkyls

A second source of borazole derivatives is provided by boron trialkyls.

Wiberg et al.[20] obtained *B*-trimethylborazole by heating an equimolar mixture of trimethylboron and ammonia at 530° for 2 h: an "ammoniate" of trimethylboron is formed in the first stage of the reaction, and this at 280° can split off a molecule of methane and change into amino(dimethyl)-borine.

This latter compound is converted into *B*-trimethylborazole with elimination of methane at 330°:

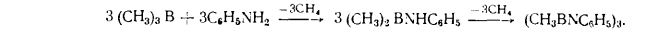


Similarly, *B*-triethylborazole is obtained in 80% yield by heating the ammonia compound of triethylboron in an autoclave at 450°[23].

The conversion of trimethylboron into borazole derivatives occurs on heating not only with ammonia but also with primary amines, though the latter require a higher temperature[24]. If the methylamine complex of trimethylboron is heated in a sealed tube at 310° for 1½ h, it is practically completely converted into dimethyl(methylamino)borine: *B*-trimethyl-*N*-trimethylborazole was obtained in 70% yield by heating this compound at 450° for 3 h.

Wiberg and his collaborators[20,24] consider that the conversion of amino(dimethyl)borine or dimethyl(methylamino)-borine into methyl derivatives of borazole takes place by their unimolecular decomposition into methane and imino-(methyl)borine, $CH_3B{=}NH$, or methyl(methylimino)borine, $CH_3B{=}NCH_3$, with subsequent trimerisation of the latter. However, no experimental data are at present available to support this mechanism.

Wiberg and Hertwig[25] studied also the reaction between trimethylboron and aniline, and concluded that heating the complex of these two compounds at 310° yields dimethyl-(phenylamino)borine, $(CH_3)_2BNHC_6H_5$, and the more volatile compound methyl(phenylimino)borine, $CH_3B{=}NC_6H_5$, which does not trimerise to *N*-triphenylborazole. They regarded this investigation as very important, supposing it to prove the existence of compounds having a double bond between boron and nitrogen atoms (so-called "borazines" in Wiberg's nomenclature) and thus supporting the mechanism of the formation of borazole and its derivatives by trimerisation of compounds of this type. However, their results relating to the preparation of methyl(phenylimino)borine, $CH_3B{=}NC_6H_5$, are incorrect. Confining themselves to measuring the vapour pressure of one of the fractions obtained in an experiment, they mistook for methyl(phenylimino)borine a mixture of aniline and dimethyl(phenylamino)borine, which have similar vapour pressures. Later Becher and Frick[26] showed that, if trimethylboron and aniline are heated at a higher temperature (at 375° for 15 h), the dimethyl(phenylamino)borine formed initially is converted into *B*-trimethyl-*N*-triphenylborazole:



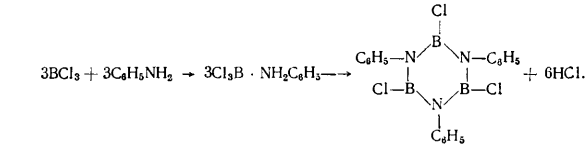
Dimethylboron fluoride also reacts with methylamine, eliminating the methyl groups to form *B*-trifluoro-*N*-trimethylborazole[27].

3. Synthesis from Boron Trichloride

Convenient methods for the preparation of borazole derivatives have been developed on the basis of boron trichloride.

Rideal[28], as early as 1889, investigated the reaction between BCl_3 and aniline, obtaining a substance giving an analysis corresponding to *B*-trichloro-*N*-triphenylborazole: he had synthesised the first compound of the borazole series, but did not establish its structure.

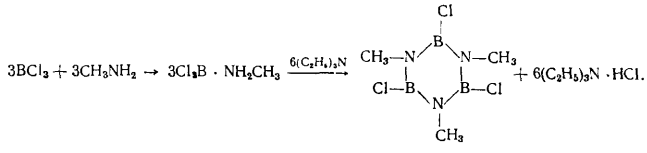
Fifty years later Jones and Kinney[29] studied this reaction in greater detail and found that addition of an equimolar quantity of aniline to a cooled solution of boron trichloride in benzene yields a complex compound which is converted into *B*-trichloro-*N*-triphenylborazole in 30% yield when the reaction mixture is subsequently boiled:



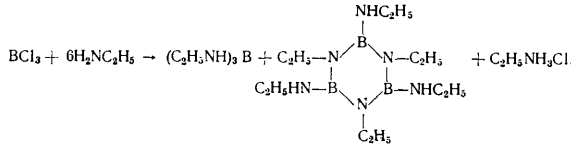
Similarly, *B*-trichloro-*N*-tri-*p*-tolylborazole[30] and *B*-trichloro-*N*-tri(*p*-methoxyphenyl)borazole[31] have been synthesised from BCl_3 and the appropriate amines. Groszos and Stafiej[32] raised the yield of *B*-trichloro-*N*-triphenylborazole to 73% by using toluene as solvent.

It is not yet possible to obtain borazole derivatives from equimolar quantities of BCl_3 and aliphatic amines. Wiberg and Hertwig[24] reported the preparation of *B*-trichloro-*N*-trimethylborazole by heating an equimolar mixture of BCl_3 and methylamine to 250°, but their product, which was not analysed, melted at 285°, whereas *B*-trichloro-*N*-trimethylborazole melts at 155°.

Borazole compounds can be obtained from BCl_3 and aliphatic amines in various ways. Thus a complex of boron trichloride and methylamine is first obtained by mixing the reactants in benzene solution; then triethylamine (2 moles) is added, and the reaction mixture boiled for 1½ h to give a 63% yield of *B*-trichloro-*N*-trimethylborazole[33]:

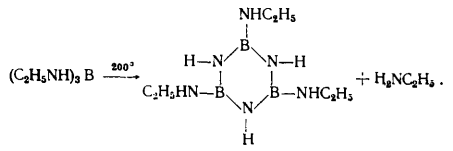


Recently Lappert[34] has found that BCl_3 (1 mole) reacts with ethylamine (6 moles) in pentane solution at -80° to yield, when the reaction products are subsequently distilled off, trisethylaminoborine (55%) and *B*-trisethylamino-*N*-triethylborazole:

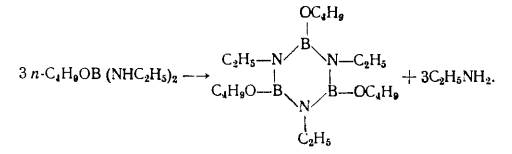


On heating the trisethylaminoborine at 200° for 3½ h,

Lappert obtained *B*-trisethylaminoborazole[34] in high yield:



He obtained[34] *B*-tributoxy-*N*-triethylborazole by pyrolysis of butoxy bis(ethylamino)borine or dibutoxy(ethylamino)-borine:

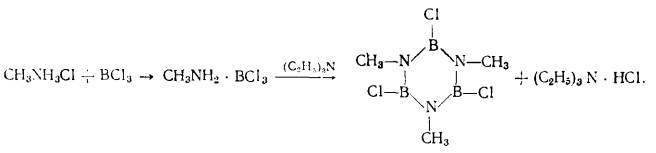


Brown and Laubengayer[35] made the interesting observation that under certain conditions boron trichloride can react with ammonium chloride to form *B*-trichloroborazole, this synthesis being accomplished in two ways. The first method consists in passing a stream of BCl_3 through ammonium chloride heated to 165°–175° in a tube. The second, simpler, method is to boil a mixture of chlorobenzene and ammonium chloride in the presence of BCl_3 vapour. In both cases the yield is 35%:

$$3NH_4Cl + 3BCl_3 \rightarrow (ClB{-}NH)_3 + 9HCl.$$

The yield of *B*-trichloroborazole can be considerably increased by treating the solid residue obtained from the previous experiment with the initial reactants[36]. The reaction is catalysed by mercury[33]. To obtain a large quantity of *B*-trichloroborazole, it is useful to employ rather more BCl_3 than is recommended by Brown and Laubengayer. The highest yield (43%) of *B*-trichloroborazole is obtained by adding BCl_3 to a suspension of NH_4Cl in chlorobenzene at a rate of 40 ml/h[33].

Hydrochlorides of primary aliphatic amines also react with BCl_3. Becher and Frick[26] obtained *B*-trichloro-*N*-trimethylborazole by Brown and Laubengayer's method from methylamine hydrochloride and BCl_3 in benzene solution. The product was purified by sublimation, but was not characterised. Turner and Warne[37] found that BCl_3 reacts with methylamine hydrochloride in benzene to form a complex $BCl_3.CH_3NH_2$, which is smoothly converted into *B*-trichloro-*N*-trimethylborazole and triethylamine hydrochloride on treatment in the cold with triethylamine:



Ethylamine and butylamine yielded with BCl_3 *B*-trichloro--*N*-triethylborazole and *B*-trichloro-*N*-tributylborazole respectively[37].

Brown and Laubengayer's method has been used to synthesise *B*-tribromoborazole by heating a mixture of ammonium bromide and boron tribromide in bromobenzene at 120°–130° for 8–12 h[36].

Borazole derivatives can be obtained starting from hydrohalides of hydrazine or an alkylhydrazine and BCl_3 or BBr_3.[38]

The mechanism of the formation of *B*-trichloroborazoles from ammonium salts and BCl_3 has not been discussed in the literature. Ammonium (or alkylammonium) tetrachloroborates are evidently formed in the first stage of the reaction, and on heating decompose into ammoniates or aminates of boron trichloride and HCl:

$$RNH_3Cl + BCl_3 \rightarrow NH_3R\,[BCl_4]^- \xrightarrow{-HCl} BCl_3 \cdot NH_3R.$$

This view of the reaction mechanism is supported by the infra-red absorption spectra of the reaction products formed by BCl_3 with amine salts, which have characteristic absorption bands in common with the spectra of potassium tetrachloroborate[39].

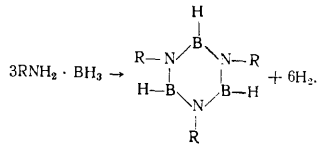
4. Synthesis from Ammonium Salts and Lithium Tetrahydroborate

A general method for obtaining borazole compounds is provided by the reaction between lithium tetrahydroborate and ammonium chloride or hydrochlorides of primary aliphatic amines, discovered by Schaeffer and Anderson[40].

To prepare *N*-trimethylborazole by this method an ethereal solution of methylamine hydrochloride and lithium tetrahydroborate is allowed to stand until hydrogen evolution ceases, and is then boiled for 3 h, the ether is distilled off, and the residue heated at 250°[40]. This technique was later simplified and applied to the preparation not only of *N*-trimethylborazole but also of other *N*-alkyl derivatives of borazole[41]. The reaction is carried out in two stages. An addition compound of borine and the amine, $BH_3.NH_2R$, is first obtained from the amine salt and $LiBH_4$ in ethereal solution at room temperature:

$$RNH_3Cl + LiBH_4 \rightarrow RNH_2 \cdot BH_3 + H_2 + LiCl,$$

and this is then decomposed at 250°–325°:



The *N*-triethyl-, *N*-tripropyl-, and *N*-triisopropylborazoles have been obtained in this way in 84–94% yield.

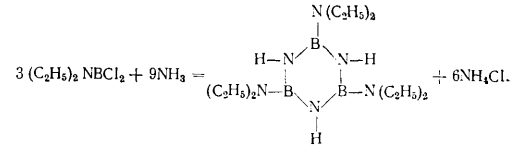
To obtain borazole, a mixture of $LiBH_4$, NH_4Cl, and broken glass is heated at 300° for 30 min[42]. The fairly low yield of borazole (30–35%) is explained by the fact that at high temperatures part of the borazole reacts with the original ammonium chloride to form *B*-chloroborazole. This method of preparing borazole has been improved and studied in detail by Mikheeva and Markina[43].

N-Triphenylborazole also has been synthesised by Schaeffer and Anderson's method[26].

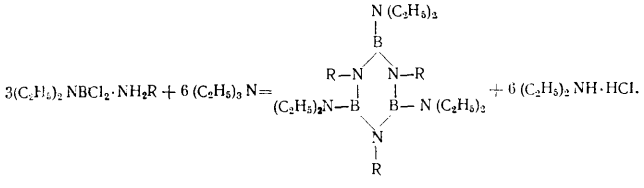
5. Synthesis from *N*-Substituted Aminoboron Dichlorides

Niedenzu and Dawson[33] have synthesised *N*-substituted *B*-triaminoborazoles by the reaction of ammonia or primary amines with *N*-substituted aminoboron dichlorides. *B*-Trisdiethylaminoborazole is formed in 52% yield by the interaction of diethylaminoboron dichloride with ammonia in

benzene solution at a low temperature:

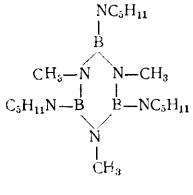


The reaction with primary amines can be conveniently carried out in two stages: a complex of diethylaminoboron dichloride with the amine is first obtained in ether, and this then reacts with triethylamine:



A 92% yield of *B*-tris(diethylamino)-*N*-trimethylborazole from diethylaminoboron dichloride and methylamine was obtained in this way, whereas the action of an excess of methylamine on diethylaminoboron dichloride gave only a 58% yield.

Similarly, *B*-tripiperidino-*N*-trimethylborazole is obtained from piperidinoboron dichloride, methylamine, and triethylamine:

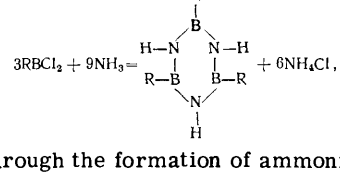


6. Synthesis from Alkyl- and Arylboron Dichlorides

A very simple and convenient method for the preparation of various alkyl and aryl derivatives of borazole is based on the use of organoboron dichlorides.

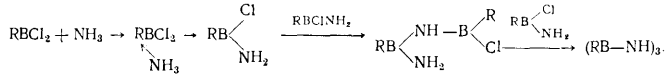
Mikhailov and Kostroma obtained a very good yield of *B*-triphenylborazole by passing ammonia into a heated benzene solution of phenylboron dichloride[44]: *B*-tri-*p*-tolyl-, *B*-tri-*p*-chlorophenyl-, and *B*-tri-*p*-bromophenylborazoles were similarly synthesised from the corresponding arylboron dichlorides[45].

The action of ammonia on isopentylboron dichloride yields *B*-triisopentylborazole[46], the reaction, expressed by the general equation



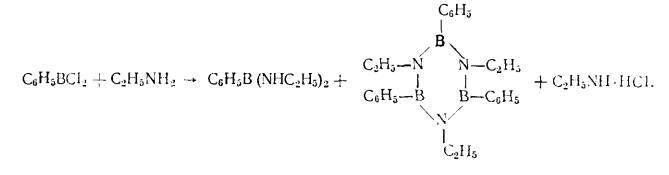
proceeding through the formation of ammoniates of the organoboron dichlorides.

The subsequent course of the reaction is probably essentially a conversion of the ammoniates into the alkyl or aryl(amino)boron chloride, the molecules of which then condense together to form *B*-trisubstituted borazole derivatives:

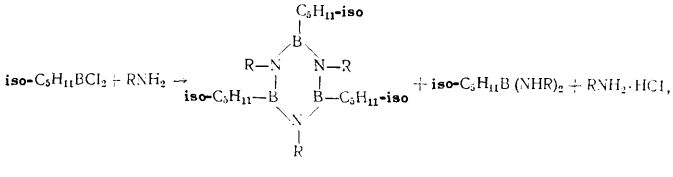


Booth and Kraus[47] obtained a substance having b.p. 100° at 0.005 mm/Hg by the action of ammonia and sodium on dibutylboron chloride, which they regarded as a polymer of butyl(imino)borine $(C_4H_9B{=}NH)_n$. This substance is not *B*-tributylborazole, since it has a higher boiling point even than *B*-triisopentylborazole[46] (115.5°/0.1). Ruigh and Gunderley[48] repeated the experiment of Booth and Kraus without using sodium, and obtained *B*-tributylborazole, but they do not give its physical properties.

The reaction between arylboron dichlorides and primary aliphatic amines is more complex. Thus ethylamine reacts with phenylboron dichloride to give a low (21%) yield of *B*-triphenyl-*N*-triethylborazole and a product in which both chlorine atoms have been replaced by alkylamino groups, namely bisethylamino(phenyl)borine (33%)[49]:

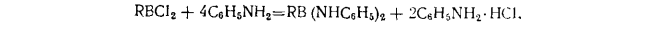


The reaction between primary aliphatic amines and alkylboron dichlorides occurs similarly, but borazole compounds are obtained in greater yield[46]. Thus ethylamine and isobutylamine react with isopentylboron dichloride to form *B*-triisopentyl-*N*-triethylborazole and *B*-triisopentyl-*N*-triisobutylborazole respectively in 50% yield, whereas the yield of the corresponding *N*-substituted diamino(isopentyl)borines amounts to 32–38%:



where R = C_2H_5, iso-C_4H_9.

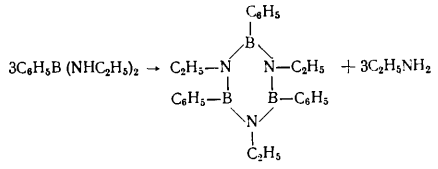
It is not possible to obtain *B*-trialkyl-*N*-triarylborazoles or *B*-triaryl-*N*-triarylborazoles directly by this method, since aromatic amines (aniline) form only *N*-substituted alkyl or aryl(diamino)borines with arylboron dichlorides[49] or alkylboron dichlorides[46]:



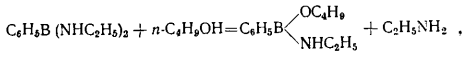
7. Synthesis from *N*-Substituted Alkyl and Aryl(diamino)borines

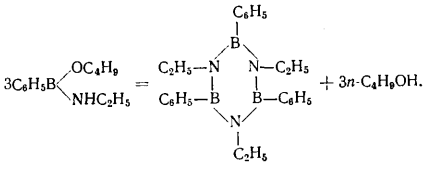
To synthesise alkyl and aryl derivatives of borazole we can use *N*-substituted alkyl- or aryl(diamino)borines formed by the action of primary amines on alkyl- or arylboron dichlorides.

Mikhailov and Aronovich[49] prepared *B*-triphenyl-*N*-triethylborazole by heating bisethylamino(phenyl)borine at 210° for 2 h:



The reaction is complicated by side reactions, and the yield is only 17%. Later it was found that the yield of *B*-triphenyl-*N*-triethylborazole can be raised to 85% if bisethylamino(phenyl)borine is heated at 260° in the presence of a small amount of n-butyl alcohol[50], which acts catalytically by forming with the original substance an aryl(ethylamino)-boric ester, which is smoothly converted into the borazole compound with elimination of the alcohol. The regenerated alcohol reacts afresh with the original organoboron amine:

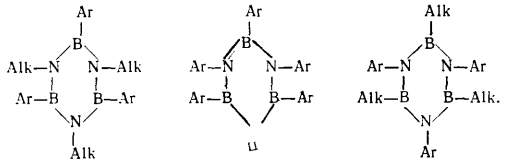




Phenylbisphenylaminoborine on heating at 270° forms hexaphenylborazole in 32% yield.

N-Arylated diamino(alkyl)borines require to be heated to a higher temperature (300°–360°). Pyrolysis of isopentylbisphenylaminoborine gives a high yield of *B*-triisopentyl-*N*-triphenylborazole[46].

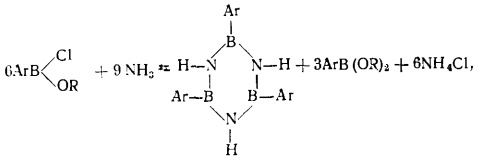
This method thus enables the following types of borazole derivatives to be prepared:



8. Synthesis from Arylchloroboric Esters

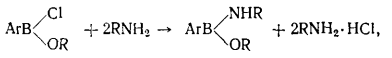
Mikhailov and Kostroma[44,50] have found that borazole derivatives can be obtained by the action of ammonia or amines on arylchloroboric esters.

When NH_3 is passed into an ethereal solution of the ester, the following reaction occurs:

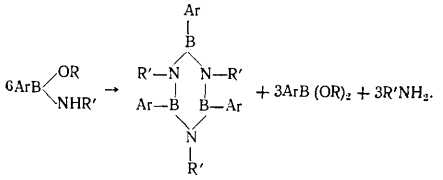


the yield of *B*-triarylborazoles being 83–87% on the basis of this equation. *B*-Triphenyl-, *B*-tri-*p*-tolyl-, and *B*-tri-α-naphthylborazoles have been synthesised in this way.

Primary aliphatic amines form aryl(alkylamino)boric esters,

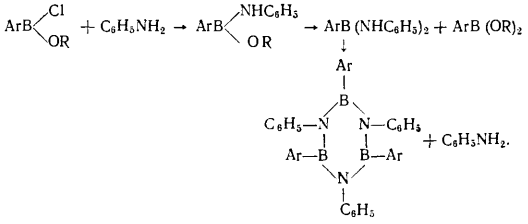


which on heating eliminate the alcohol and are converted into *B*-triaryl-*N*-trialkylborazoles:



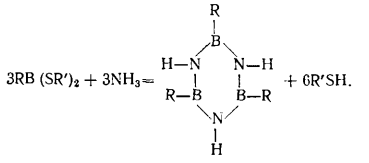
Under the influence of the resulting alcohol, half of the original amino ester is converted into an arylboric ester and the corresponding amine.

With aniline, aryl(phenylamino)boric esters are formed which on heating (200°) symmetrise into arylboric esters and *N*-phenylated diamino(phenyl)borines. The latter, as already indicated above, give on heating to 270°–400° a 30–35% yield of hexaarylborazoles:



9. Synthesis from Organothioboric Esters

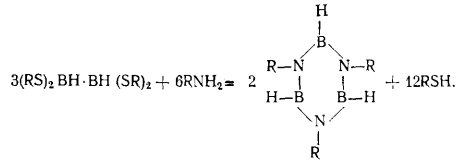
Mikhailov et al.[51] have found a simple and general method for preparing borazole derivatives in the reaction between esters of alkyl- or arylthioboric acids and ammonia, enabling *B*-trialkyl- and *B*-triarylborazoles to be prepared in yields of 85–95%:



10. Synthesis from Tetraalkylthiodiboranes

A convenient method of obtaining *N*-alkylated borazoles, discovered by Mikahilov and Shchegoleva[52], is the action of

primary amines on tetralkylthiodiboranes at room temperature:



N-Triethyl- and *N*-tributylborazoles have been synthesised by this method in yields of 66–77%.

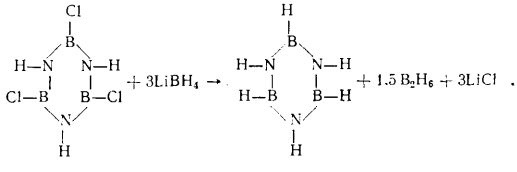
II. SYNTHETIC METHODS BASED ON REACTIONS OF FUNCTIONAL DERIVATIVES OF BORAZOLE

The investigation of the chemical properties of several compounds has led to the development of synthetic methods based on reactions of functional derivatives of borazole.

1. Synthesis of Borazole and its Derivatives from *B*-Chlorinated Borazoles

The study of the chemical properties of *B*-chlorinated borazoles has shown that the chlorine atoms are reactive, and can be displaced by hydrogen and various radicals.

Schaeffer et al.[36] found that all three chlorine atoms are replaced by hydrogen in the reaction of lithium tetrahydroborate with *B*-trichloroborazole in dibutyl ether:



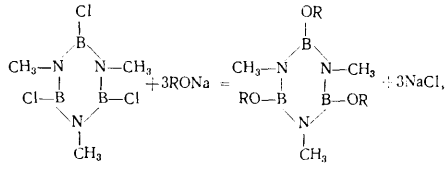
This reaction enables large quantities to be prepared with a 65% yield.

Reduction of *B*-trichloro-*N*-triphenylborazole with lithium tetrahydroaluminate in ethereal medium gives an 85% yield of *N*-triphenylborazole[53].

The possibility of obtaining borazole derivatives by reducing its *B*-trichloro derivatives with lithium tetrahydroborate was pointed out by Hohnstedt and Haworth[54], but no experimental details were given.

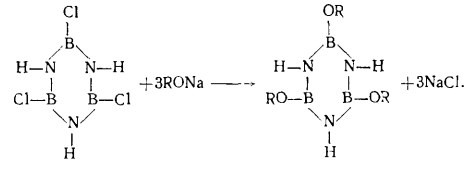
It is possible to replace chlorine atoms by hydroxy groups in a few cases. Thus *B*-trichloro-*N*-triphenylborazole[29] and *B*-trichloro-*N*-tri-*p*-methoxyphenylborazole[31] react with three molecules of water to form the corresponding *B*-trihydroxy derivatives, whereas the analogous *B*-trichloro-*N*-tri-*p*-tolylborazole is decomposed by moist benzene[30].

The *B*-alkoxy and *B*-phenoxy derivatives of borazole cannot be obtained by the action of alcohols or phenol on *B*-trichloro-*N*-trimethylborazole[55], methylamine hydrochloride and an alkyl or phenyl borate being formed. However, the chlorine atoms in this borazole compound can be replaced by alkoxy or phenoxy groups comparatively smoothly (in 43–58% yield) by the action of alcoholates of primary alcohols or a phenate in benzene solution. With alcoholates of secondary or tertiary alcohols, the yield of *B*-trialkoxy-*N*-trimethylborazoles is only 14–20%:



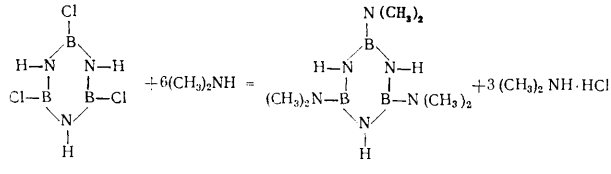
where R = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, t-C_4H_9, C_6H_5.

Haworth and Hohnstedt[56] replaced the chlorine atoms in *B*-trichloroborazole by alkoxy groups by means of alcoholates . Thus sodium methylate reacts with *B*-trichloroborazole in boiling chlorobenzene to give a 54% yield of *B*-trimethoxyborazole, and with sodium ethylate *B*-triethoxyborazole is formed:

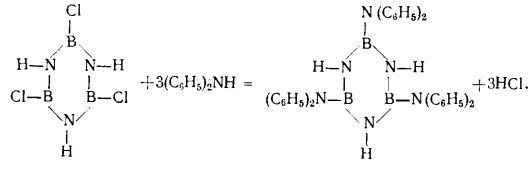


The chlorine atoms in *B*-trichloroborazole can be exchanged for alkylamino groups by the action of primary and secondary amines.

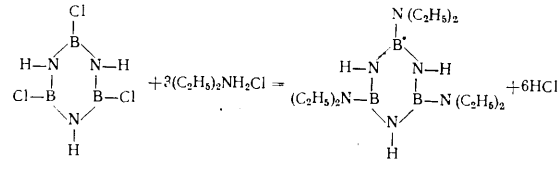
Gould[57] prepared *B*-tris(dimethylamino)borazole by the action of an excess of dimethylamine on *B*-trichlorborazole:



With diphenylamine the reaction can be carried out with the reactants in stoichiometric proportions[33]:



The chlorine atoms in *B*-trichloroborazole can be exchanged for diethylamino groups also by heating with diethylamine hydrochloride in tetrahydrofuran, but the yield of the resulting *B*-tris(diethylamino)borazole is low:

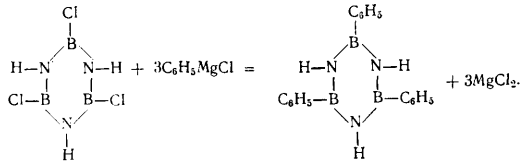


Gould[57] points out that *B*-trichloroborazole reacts with liquid ammonia to form *B*-triaminoborazole, but the properties of this compound are not given.

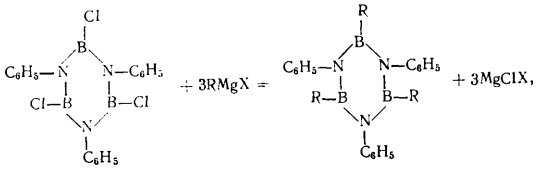
B-Trichloroborazole can react with diazomethane, yielding *B*-trischloromethylborazole[58].

B-Trichloro derivatives of borazole react with Grignard reagents.

Becher and Frick[26] synthesised *B*-triphenylborazole by the action of phenylmagnesium chloride on *B*-trichloroborazole. They obtained also *B*-triphenyl-*N*-trimethylborazole from *B*-trichloro-*N*-trimethylborazole and phenylmagnesium chloride:

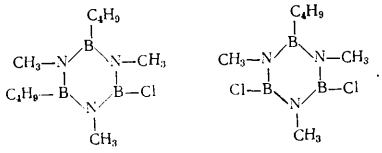


Groszos and Stafiej[32] synthesised various derivatives of borazole from *B*-trichloro-*N*-triphenylborazole and organomagnesium compounds, achieving yields of 65–84%. The yield of hexaphenylborazole is considerably worse with phenyllithium than with phenylmagnesium bromide:



where R = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, iso-C_4H_9, C_6H_5, $CH_2{=}CH{-}CH_2$.

Exchange of chlorine atoms for alkyl groups occurs smoothly by reaction of Grignard reagents with *B*-trichloro-*N*-trimethylborazole. Ryschkewitsch et al.[59] synthesised *B*-triethyl-, *B*-triallyl-, and *B*-tributyl-*N*-trimethylborazole in this way. They found that when butylmagnesium chloride (2 moles) acts on *B*-trichloro-*N*-trimethylborazole (1 mole), the fully alkylated product is accompanied by the products of partial substitution, *B*-dibutyl-*B*-chloro-*N*-trimethylborazole and *B*-butyl-*B*-dichloro-*N*-trimethylborazole:

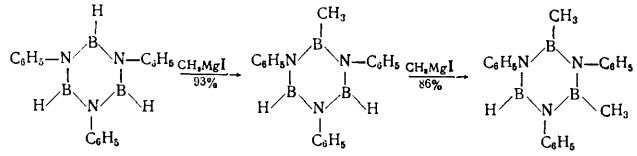


2. Synthesis of Borazole Derivatives from *N*-Alkyl and *N*-Aryl Borazoles

Smalley and Stafiej[53] made the interesting discovery that the hydrogen atoms in *N*-substituted borazoles are replaceable by alkyl or aryl groups by reaction with organomagnesium or organolithium compounds.

The action of three moles of the organometallic compound on one mole of *N*-triphenylborazole produced high yields of *B*-trimethyl-, *B*-tributyl-, and *B*-triphenyl-*N*-triphenylborazole. *B*-Alkylation of *N*-trimethylborazole yielded hexamethylborazole (83%). Yields of 49–61% of *B*-triphenyl-*N*-trimethylborazole were obtained by the action of phenyllithium or of phenylmagnesium bromide on *N*-trimethylborazole.

Replacement of hydrogen atoms in *N*-trisubstituted borazole can be carried out in stages, the action of 1 mole of CH_3MgI on *N*-triphenylborazole giving a 93% yield of *B*-methyl-*N*-triphenylborazole, which is smoothly converted by a second mole of CH_3MgI into *B*-dimethyl-*N*-triphenylborazole. Similar results are obtained by using phenylmagnesium bromide.



Stepwise replacement of hydrogen atoms can be accomplished also in *N*-trimethylborazole.

Partial substitution products can be used to synthesise derivatives having different groups linked to the boron atoms. For example, Smalley and Stafiej prepared *B*-methyl-*B*-ethyl-*B*-propyl-*N*-triphenylborazole by the following series of reactions:

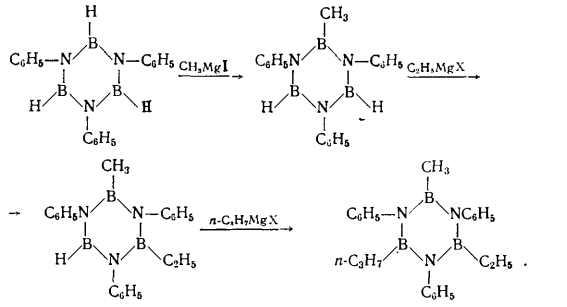


TABLE 1. Borazole and its alkyl derivatives.

Compound	B.p.	M.p.	n_D^{20}	d^{20}	Reference
Borazole	55	—58	1.3821	0.8419	7,11,36
B-Methylborazole	87[a]	—59			21
N-Methylborazole	84[a]				10
B-Dimethylborazole	107[a]	—48			21
N-Dimethylborazole	108[a]				10
B-Methyl-*N*-methylborazole	124[a]				10
$(CH_3B{-}NH)_3$	127	31.8			20,21
$(HB{-}NCH_3)_3$	134	—9	1.4404	0.8519	10,20,40,41
B-Dimethyl-*N*-methylborazole	139[a]				10
B-Trimethyl-*N*-methylborazole	158[a]				10
B-Methyl-*N*-trimethylborazole	162,5[a]				53
B-Dimethyl-*N*-trimethylborazole	187[a]				53
$(CH_3B{-}NCH_3)_3$	221	99			24,53
$(C_2H_5B{-}NH)_3$	67/7	—54			23
$(HB{-}NC_2H_5)_3$	68/20	—49.6	1.4384	0.8433	41,52
$(HB{-}NC_3H_7\text{-}n)_3$	225		1.4484	0.8347	41
$(HB{-}NC_3H_7\text{-}iso)_3$	203	—6.5	1.4443	0.8476	41
$(HB{-}NC_4H_9\text{-}n)_3$	80/0.25		1.4515	0.8426	52
$(iso\text{-}C_5H_{11}B{-}NH)_3$	115.5/0.1		1.4538	0.8485	46,51
$(C_2H_5B{-}NCH_3)_3$	98/1.8	2	1.4791[b]		59
$(n\text{-}C_4H_9B{-}NCH_3)_3$	140/1.1	—17	1.4759[b]		59
$(iso\text{-}C_5H_{11}B{-}NC_2H_5)_3$	114/0.06	45			46
$(iso\text{-}C_5H_{11}B{-}N{-}C_4H_9\text{-}n)_3$	128/0.06				46
$(CH_2{=}CH{-}CH_2B{-}NCH_3)_3$	112/1.3	—37	1.5047[b]		59
$(ClCH_2B{-}NH)_3$	125/0.01[c]	178			58

(a) By extrapolation of vapour-pressure data; (b) $n_D^{22.5}$; (c) temperature of sublimation.

TABLE 2. Alkyl-aryl borazole derivatives.

Compound	M.p., °C	Reference	Compound	M.p., °C	Reference
B-Methyl-*N*-triphenylborazole	142	53	$(CH_2{=}CH{-}CH_2B{-}NC_6H_5)_3$	99	32
B-Dimethyl-*N*-triphenylborazole	206	53	*B*-Methyl-*B*-ethyl-*N*-triphenylborazole	128	53
$(CH_3B{-}NC_6H_5)_3$	270	32, 53	*B*-Dimethyl-*B*-n-butyl-*N*-triphenylborazole	113	53
$(C_2H_5B{-}NC_6H_5)_3$	171	32	*B*-methyl-*B*-ethyl-*B*-n-propyl-*N*-triphenylborazole	131	53
$(n\text{-}C_3H_7B{-}NC_6H_5)_3$	171	32	$(C_6H_5B{-}NCH_3)_3$	249	26
$(iso\text{-}C_3H_7B{-}NC_6H_5)_3$	198	32	$(C_6H_5B{-}NC_2H_5)_3$	209	49, 50
$(n\text{-}C_4H_9B{-}NC_6H_5)_3$	132	32	$(p\text{-}CH_3C_6H_4B{-}NC_2H_5)_3$	221	50
$(iso\text{-}C_4H_9B{-}NC_6H_5)_3$	187	32	$(\alpha\text{-}C_{10}H_7B{-}NC_2H_5)_3$	271	44
$(iso\text{-}C_5H_{11}B{-}NC_6H_5)_3$ *	95.5	46			

* B.p. 181°/0.03.

TABLE 3. Aryl derivatives of borazole.

Compound	M.p., °C	Reference	Compound	M.p., °C	Reference
$(HB{-}NC_6H_5)_3$	161	26, 53	*B*-Phenyl-*N*-triphenylborazole	215	53
$(C_6H_5B{-}NH)_3$	182	26, 44, 51	*B*-Diphenyl-*N*-triphenylborazole	207	53
$(p\text{-}CH_3C_6H_4B{-}NH)_3$	190	44, 45	$(C_6H_5B{-}NC_6H_5)_3$	415	32, 49, 50
$(p\text{-}ClC_6H_4B{-}NH)_3$	270	45	$(p\text{-}CH_3C_6H_4B{-}NC_6H_5)_3$	284	50
$(p\text{-}BrC_6H_4B{-}NH)_3$	293	45			
$(\alpha\text{-}C_{10}H_7B{-}NH)_3$	187	44			

TABLE 4. Halogenated borazole derivatives

Compound	B.p., °C	M.p., °C	Reference
B-Chloroborazole	109.5[a]	−34.6	42
B-Bromoborazole	122.3[a]	−34.8	42
B-Dichloroborazole	151.9[a]	33.5[a]	42
B-Dibromoborazole	167.1[a]	50	42
$(ClB{-}NH)_3$		84.5	33, 36
$(BrB{-}NH)_3$		128	36
$(FB{-}NCH_3)_3$	224	85	27
$(ClB{-}NCH_3)_3$	120—130/0.1—1[b]	155	37, 59
$(ClB{-}NC_2H_5)_3$		57	37
$(ClB{-}NC_4H\text{-}p)_3$[e]	120 0.5	~30	37
B-Di-n-butyl-*B*-chloro-*N*-trimethylborazole	122/1.13[c]		59
B-n-butyl-*B*-dichloro-*N*-trimethylborazole	101/1.1[d]	− 4	59
$(ClB{-}NC_6H_5)_3$		272	29
$(ClB{-}NC_6H_4CH_3\text{-}p)_3$		309	30
$(ClB{-}NC_6H_4OCH_3\text{-}p)_3$		235	31

(a) By extrapolation of vapour-pressure data.

(b) Sublimation temperature.

(c) $n_D^{22.5}$ 1.4008.

(d) $n_D^{22.5}$ 1.4876.

(e) Probably $(ClB-NC_6H_4CH_3\text{-}P)_3$ (Ed. of Translation).

TABLE 5. Oxygen and nitrogen derivatives of borazole.

Compound	B.p., °C	M.p., °C	n_D	Reference
$(HOB{-}NC_6H_5)_3$		95—130		29
$(HOB{-}NC_6H_4OCH_3\text{-}p)_3$		112—120		31
$(CH_3OB{-}NH)_3$		111		56
$(C_2H_5OB{-}NH)_3$		54		56
$(CH_3OB{-}NCH_3)_3$	65/0.07		1.4610[a]	55
$(C_2H_5OB{-}NCH_3)_3$	80.5/0.1		1.4540[b]	55
$(n\text{-}C_3H_7OB{-}NCH_3)_3$	103/0.15		1.4561[c]	55
$(iso\text{-}C_3H_7OB{-}NCH_3)_3$	87/0.1		1.4460[d]	55
$(n\text{-}C_4H_9OB{-}NCH_3)_3$	134/0.3		1.4572[a]	55
$(n\text{-}C_4H_9OB{-}NC_2H_5)_3$	156/0.4		1.4544[e]	34
$(t\text{-}C_4H_9OB{-}NCH_3)_3$	125/0.52	87		55
$(C_6H_5OB{-}NCH_3)_3$	187/0.07	84		55
$(H_2NB{-}NH)_3$		85—105		57
$(CH_3NHB{-}NH)_3$		112		33
$[(CH_3)_2NB{-}NH]_3$				33, 57
$[(C_2H_5)_2NB{-}NH]_3$	150/7	>300		33
$[(C_6H_5)_2NB{-}NH]_3$		84		33
$[(C_2H_5)_2NB{-}NC_2H_5]_3$				33
$[(C_6H_5)_2NB{-}NC_2H_5]_3$	95/3			33
$(C_2H_5NHB{-}NC_2H_5)_3$	150/0.1		1.4826[f]	34

(a) n_D^{23}; (b) $n_D^{22.5}$; (c) n_D^{22}; (d) n_D^{23}; (e) n_D^{20}, d^{20} 0.935; (f) n_D^{20}, d^{20} 0.933.

The properties of borazole and its substitution products are listed in Table 1, those of its alkyl-aryl derivatives in Table 2, of its aryl derivatives in Table 3, of halogenated derivatives in Table 4, and the properties of oxygen and nitrogen derivatives of borazole are listed in Table 5.

III. PROPERTIES OF BORAZOLE AND ITS DERIVATIVES

Stock and Pohland[7], on the basis of their experiments with a small quantity of gaseous borazole, considered it to be a stable compound, undergoing no changes in the course of several months. Schaeffer et al.[36] found, however, that borazole in the liquid state, even when kept at -80° for a few days, decomposed appreciably, traces of a colourless non-volatile precipitate separating out. When kept at room temperature for a few weeks, borazole evolves a considerable quantity of hydrogen together with a small amount of diborane and other volatile products. Borazole is more stable in the gaseous state.

Borazole and the majority of its derivatives react in air, and all manipulations with it are therefore carried out in dry nitrogen. The aryl derivatives of borazole possess the greatest stability in air. Thus, for example, *B*-triphenyl-*N*-triethylborazole and hexaphenylborazole can be kept in an open vessel for a long time[49].

Wiberg and Bolz[11] found that at room temperature borazole forms 1 : 3 molecular compounds with water, methyl alcohol, and HBr. According to their data, the methanol compound, imino(methoxy)borine, $CH_3OB{=}NH$, which represents a monomeric form of *B*-trimethylborazole. This statement of Wiberg and Bolz is incorrect. According to Haworth and Hohnstedt's results[56], the complex of borazole with three molecules of methanol evolves hydrogen on heating and is converted into the ammoniate of trimethyl borate $[(CH_3O)_3B.NH_3]$, *B*-trimethoxyborazole, and a non-volatile solid of indefinite composition. The latter workers found that with ethanol, borazole forms an adduct, $B_3N_3H_6 \cdot 3C_2H_5OH$, which is unstable and even at -30° is partly converted into NH_3, ethyl borate, and a solid, which at 100° is partly converted into *B*-triethoxyborazole.

NH_3, ethyl borate, and a solid, which at 100° is partly converted into *B*-triethoxyborazole.

According to Wiberg and Bolz[11] at 100° the complex compound of borazole with HBr splits off hydrogen and is converted into tribromoborazole, whereas the action of bromine on borazole yields dibromoborazole: the physical properties of these compounds were not described.

At room temperature borazole reacts with boron trichloride and tribromide forming the corresponding mono- and dihalogenated borazoles[42], hydrogen, and non-volatile solid products. Borazole reacts with amino(dimethyl)borine to form methane and mono-, di-, and trimethylborazoles[21].

At 100° borazole can react with trimethylboron, forming *B*-methyl-, *B*-dimethyl-, and *B*-trimethylborazoles[10].

The majority of borazole derivatives, like borazole itself, are hydrolysed on heating with water, methylboric acid and ammonia being formed from *B*-trimethylborazole, and boric acid, methylamine, and hydrogen from *N*-trimethylborazole[20]. Hexamethylborazole yields methylboric acid and methylamine on hydrolysis[24].

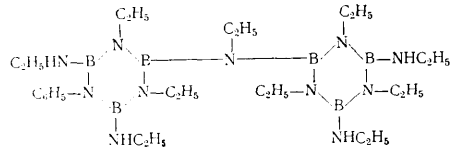
At 100° *B*-triphenyl-*N*-trimethylborazole is smoothly decomposed under the influence of water into methylamine and phenylboric acid[53], whereas under similar conditions *B*-trimethyl-*N*-triphenylborazole does not undergo any change[53].

At 45° *B*-trimethylborazole forms with hydrogen chloride a non-volatile, colourless, solid compound[20], which is regarded as a product of the addition of three molecules of HCl to the original compound[20]. According to Wiberg and Hertwig[24], hexamethylborazole at 90° forms with HCl an addition compound containing three molecules of HCl, but this compound was not identified analytically. At 150° hexamethylborazole is converted by HCl into methylboron dichloride and methylamine hydrochloride.

N-Methylborazole reacts at 100° with trimethylboron forming *B*-methyl-*N*-methyl-, *B*-dimethyl-*N*-methyl-, and *B*-trimethyl-*N*-methylborazoles, and hydrogen[10].

The ability of *N*-substituted derivatives of borazole to react with Grignard reagents, as well as the reactivity of *B*-halogenated borazoles, has been discussed in section II.

At 200° *B*-trisethylamino-*N*-triethylborazole eliminates ethylamine and is converted into a condensation product which has been given the following structure:



Further heating at 600° converts this product into a polymer, which is hydrolysed by hot water to boric acid and ethylamine[34].

B-Trimethoxyborazole reacts with methanol at 100° to form the ammoniate of trimethyl borate[56]. Pyrolysis of *B*-trimethoxyborazole yields traces of the ammoniate of trimethyl borate and a non-volatile solid[56].

Investigations have been made of the ultra-violet spectra of borazole[60,61], *B*-trimethyl-, *N*-trimethyl-, *B*-trichloro-[62], *B*-triphenyl-[63,64], *B*-tri-*p*-chlorophenyl-[64], *N*-triphenyl-, *B*-triphenyl-, and *B*-trimethyl-*N*-triphenylborazoles[63].

Studies have been made also of the infra-red spectra of borazole[26,65] and several of its derivatives: *B*-trimethylborazole[66] and *B*-triphenyl-, *N*-triphenyl-, *B*-trimethyl-*N*-triphenyl-, *B*-triphenyl-*N*-trimethyl-, *B*-trichloro-, *B*-trichloro-*N*-triphenyl-, and *B*-trichloro-*N*-trimethylborazoles[26].

The Raman spectra of borazole[65] and *B*-trimethylborazole[67] have been studied.

X-Ray and electron diffraction methods have been used to determine interatomic distances in borazole[9] (N–B bond length 1.44 Å), *B*-trichloroborazole[68-70] (1.41 Å), and *N*-trimethylborazole[70] (1.42 Å).

The heat of formation of *B*-trichloroborazole has been determined[71].

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DEVELOPMENT IN THE SYNTHESIS AND APPLICATION OF ION EXCHANGE AND ELECTRON EXCHANGE RESINS

S. E. Bresler

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INTRODUCTION

The introduction of cross-linked polymeric electrolytes – ion exchange resins – has provided an entirely new approach to many problems of purification and separation of chemically similar substances, i.e. to the central problems of analytical and preparative chemistry. The first problems to be solved in this way concerned desalting or deionisation of industrial solutions, e.g. in the sugar industry, the production of drinking water from sea water, or the substitution of undesirable ions by acceptable ones, e.g. calcium and silicate in boiler water by sodium and hydroxide.

Problems such as these make very simple demands of an ion exchanger. Selectivity for a particular ion is not required. On the contrary the polymer must be a general purpose absorber of a wide range of ions.

Much more sophisticated problems arise in separating individual substances from complex natural or industrial products. The introduction of polymeric ion exchangers in conjunction with chromatographic methods has brought about a real revolution in this field. It should be remembered that while chromatography is an exceptionally selective method of separation, it is lengthy and comparatively inefficient in terms of unit volume or cross-section of the apparatus (ion-exchange columns). Ion exchange and chromatography are therefore best used in analysis and in small scale synthesis. The extraction and purification of rare, highly dispersed, and radioactive elements, and the separation of stable isotopes are the fields of industrial inorganic chemistry in which the use of ion exchange and chromatography is expedient. As far as the polymeric materials are concerned, the chief problem here is to make selective absorbents which have at least a group specificity, and preferably an individual specificity for given elements.

In the organic chemical industry the most important applications of ion exchange and chromatography are related to the production of valuable small-tonnage products of complex nature – antibiotics, vitamins, hormones, alkaloids, active protein preparations (antigens, antibodies, enzymes, viruses, baceteriophages). In these cases, the advantages of the ion exchange method are used to the full; it is the most "gentle" of all preparative methods, and enables particularly sensitive and labile organic compounds to be purified and concentrated. Applications of ion exchange in organic chemical technology make special demands on the synthesis of ion-exchange resins. As in the previous case, high selectivity for individual ions is involved. In addition, the large dimensions of organic ions, containing various functional groups, pose additional problems in the synthesis of resins suitable for their separation and purification.

The use of polymeric resins as reagents in chemical reactions is a new field of application that has emerged recently. Cations and anion-exchange resins are used successfully as catalysts in reactions requiring acidic or basic catalysts. Special electron-exchange resins, i.e. polymers able to undergo reversible oxidation-reduction, are used as reagents for the oxidation or reduction of a given material; contamination of the product by extraneous matter, which occurs when the usual oxidising and reducing agents are used, is thus avoided. These are the most important aspects of the applications of ion-exchange and electron-exchange resins.

In the present review we shall deal with several new developments in the synthesis of polymeric materials that appear to offer prospects of industrial utilisation. But, since the polymers cannot be considered in isolation from the technological methods of purification and fractionation by sorption, we shall begin with a short review of new ion--exchange and chromatographic methods.

1. DEVELOPMENT OF ION-EXCHANGE AND CHROMATOGRAPHIC METHODS

Methods for the removal of all electrolytes (deionisation) have developed in two directions. Since deionisation with ion-exchange filters involves periodic regeneration (e.g. with alkali or acid), which accounts for the main cost of the process, two types of ion-exchange processes not requiring regeneration have been devised. The first of these is the widely known method of electrodialysis through ion-exchange membranes[1,2]. Cation- and anion-exchange membranes are selectively permeable to cations and anions respectively. At present, electrodialysis consumes fairly large quantities of electrical energy, the chief source of loss being the considerable resistance of the desalted water in the cells, which are 2–5 mm thick. The membranes themselves, some 0.5 mm thick, also have an appreciable resistance (about 20% of the total resistance of the apparatus). As a result, the energy consumed in desalting sea water to produce drinking water (e.g. decreasing the salt concentration from 2.5 to 0.025%) is about 5–8 kWh ton^{-1}.

The efficiency of a multicell electrodialysis system, i.e. the ratio of the power ideally required to remove the salts (as given by thermodynamics) to that actually required, is 10–15%. Consequently, there is great scope here for further improvement, both in construction of the apparatus and in perfection of the membranes – by making membranes that are simultaneously thinner and stronger. Ion-exchange membranes can be synthesised in two ways. The first involves binding powdered resins with various polymers, with subsequent curing ("vulcanisation") of the films thus obtained (heterogeneous membranes). The second method is the direct chemical synthesis of ion-exchange membranes from suitable polymer films (homogeneous membranes). Thus polyethylene film, with polystyrene grafted to it by irradiation, was the starting material for the synthesis of sulphonic acid cation-exchange membranes and others[3].

At the present time, electrodialysis through ion-exchange membranes has found wide application in the production of drinking water, for example on ships. It is also used successfully in the technology of antibiotics and other organic substances, for demineralising solutions, for exchanging cations or anions, and for varying pH without introducing alkali or acid. Ion-exchange membranes have interesting applications in chemical analysis, particularly in automatic plant control. With their aid, electrodes may be set up for continuous measurement of the concentration of any particular ion in a solution (e.g. sodium, ammonium, chloride, sulphate, etc. electrodes), through their concentration--dependent potential, in the same way that the hydrogen electrode is used to measure hydrogen ion concentration[4]. Such electrodes are stable, have a low inertia (equilibrium potential is established in fractions of a minute), and have a good electrical conductivity, which facilitates measurements of potential. There is no doubt that ion exchange membranes will be increasingly used in the future.

The second method of deionisation, especially applicable to solutions of non-electrolytes or weak electrolytes, and not requiring periodic regeneration of the ion exchanger, has been named "ion exclusion"[5,6]. This procedure is efficient for very heavily salted solutions of weakly dissociated substances, since the ion exchanger immediately absorbs the non-ionised component while the electrolyte is excluded and passes through the filter unabsorbed. The ion-exclusion method is based on the Donnan equilibrium. The ion-exchange filter, through which the solution to be demineralised passes, contains the same ion that is to be removed. For example, if demineralisation involves removal of NaCl, the filter is filled with the sodium form of a sulphonic acid cation exchanger; the degree of swelling of the resin is such that its particles contain 50% of water. Owing to the Donnan equilibrium, which is always set up when there is a cation free to diffuse (in this case Na^+) and a fixed anion (in this case the macro-anion of the resin), or vice versa, the concentration of NaCl in the liquid within the particles of ionite will be several times smaller than in the solution (sometimes, tens of times smaller).

According to the Donnan-equilibrium theory, the efficiency of the process, i.e. the ratio of the salt concentrations outside and inside the swollen ion exchanger, increases with decrease in salt concentration. The weakly dissociated component is distributed almost equally between the solution and the swollen resin. This results in an appreciable, though not very large, capacity of the ionite for a non-ionic component (e.g. for ethanol, the capacity in practice is about 0.5 mmole g^{-1}, whereas ion-exchange capacity is about 5 mg-equiv. g^{-1}).

The ion-exclusion process is carried out by passing an aqueous solution of the original mixture through the filter. The unionised component is held in the ion exchanger, while the salt is excluded from the particles and is removed from the filter. The non-ionic component is washed from the resin with water, and the cycle is repeated. With correct operation, both the salt solution and the non-ionised solution can be obtained without appreciable dilution. However, desalting is incomplete after a single cycle and the process generally needs to be repeated several times.

Ion exclusion has been successfully used to separate acetic from hydrochloric acid, boric acid from sodium chloride, amino acids from ammonium chloride, ethyl alcohol and ethylene glycol from sodium chloride, and so on[7]*. The usual swelling, strongly basic cation exchangers are suitable for the ion-exclusion process.

We shall now turn to processes for separating individual ions from complex mixtures. Chromatographic methods, using ion-exchange sorbents, are suitable for this purpose.

Of the three alternative methods of chromatography – frontal, elution, and displacement – the first is best suited to industrial applications, because it is extremely simple technologically and is economic in the use of the exchanger. In this method, the ion-exchange filter becomes saturated exclusively with the required ion, while the others pass through unabsorbed; it is essentially a one-stage process. Ion exchangers of high selectivity are required. Normal ion-exchange resins have exchange constants for different ions that do not differ much from unity and do not exceed 10, and, as a rule, ion exchangers of this kind are unsuitable for frontal separations. However, it has been found possible to synthesise ion exchangers having exchange constants for particular ions of the order of 10^5–10^6. With

* These cases do not appear to be mentioned in references 5–7 (Ed. of Translation).

such resins, frontal analysis can be carried out for analytical and preparative purposes. Success in this method depends entirely on the synthesis of suitable ion exchangers, a matter to which we shall return later.

We consider next developments in elution chromatography, in which the main difficulty has been diffusion of the zones and a consequent fall in concentration of the components in them. This drawback almost made elution chromatography valueless. It has been overcome by a procedure which sharpens the chromatographic zones. This procedure involves setting up a concentration gradient of eluent along the column; the result, as theory shows, is that the effective sorption isotherm of the components being separated becomes curved and the zones are sharpened. In order to create a concentration gradient of eluting electrolyte, the concentration of the solution supplied to the column is gradually varied by means of an automatic dispenser[8,9].

With small columns, it is sometimes possible to set up such a concentration gradient by applying an electric field and passing a current along the chromatographic column. Gradient-elution chromatography has been applied to the analysis of particularly complex multi-component mixtures. An example is the quantitative analysis of a mixture of twenty-five amino acids, carried out fully automatically[10].

Another example is the separation of radioactive elements, in particular the transuranium elements, on micro--columns (cross-section of 1 mm^2), using complexing acids as eluents (e.g. lactic, α-hydroxyisobutyric, etc.). In all cases mentioned, sharpening of the chromatographic zones was achieved by means of a pH gradient along the column. With micro-columns, an electric field may be used for this purpose[11]. The method can be used for preparative purposes, but only for particularly valuable substances, produced in comparatively small quantities (e.g. the purification of insulin).

Finally, we consider a recent development in chromatographic methods – a new version of displacement chromatography, in which this apparently discontinuous method has been converted to continuous operation, with all the technological advantages that this entails. Such a procedure is advantageous for the separation of ions very closely similar in properties, e.g. isotopes. Its efficacy has been demonstrated by the separation of the nitrogen isotopes[12]. A series of columns that can be connected together in different ways are filled with ion exchanger. A zone of the substances to be separated is then introduced into the first column and is moved forward by a solution of the displacing ion. Both the original ionic form of the resin and the displacing ion are selected in accordance with theory so that the boundaries of the mixed zone will remain sharply defined. The zone will then be stationary and its length will not change as it moves. During the process, the zone passes from one column to another. As a column is freed, the ion exchanger in it is rapidly regenerated and the column is again included in the process, which thus proceeds continuously; as the zone passes from one column to another, products are withdrawn from both ends of the zone, and more starting material is injected.

In our laboratory a detailed theory of continuous chromatography with withdrawal of products has been worked out[13] and a separation of the alkali metals, difficult to achieve by other methods, has been carried out. For the separation of the Li–Na pair, a zone 40 cm long was used to separate a mixture consisting of 50% Li and 50% Na. It moved at a rate of 0.004 cm sec^{-1} and an equilibrium distribution was established after a distance of 1.5 m. After this, withdrawal of products started. If products of 99.9% purity are withdrawn, the rate of withdrawal of each component is 25% of the total flow in the column. The only important requirement of the resin is rigidity, i.e. a small volume change on passing from one cycle to another. The sulphonic resin SBS-1 was found quite satisfactory. The method of continuous chromatography may prove very useful in the separation of closely similar substances.

2. NEW TRENDS IN THE SYNTHESIS OF ION-EXCHANGE MATERIALS FOR INORGANIC IONS

We shall consider three important ways of synthesising ion-exchange materials. Firstly, the synthesis of organic polymeric resins. Together with the traditional methods for making polymeric acids and bases of different strengths, a completely new route has emerged – the synthesis of exchangers containing groups able to form internal complexes (chelates) with particular ions. The application of this principle, which means that in the ion exchange process chemical donor-acceptor interaction between sorbent and sorbate is involved as well as electrostatic forces, results in enormous ion-exchange constants and high selectivity.

The second method, which is also being intensively elaborated, is based on inorganic polymers, formed mainly by the elements of the Fourth Group (e.g., zirconium or titanium). Various functional groups are easily attached to the polymer chain, consisting of atoms of zirconium and oxygen or titanium and oxygen. The possibility is thus presented of obtaining a large variety of ion-exchange materials able to complex with different ions, and making possible separation of elements by frontal analysis.

The third method is extremely important for producing exceptionally mildly acting exchangers, which can adsorb, reversibly and without deactivation, such complex organic substances as proteins and even viruses. The method uses cellulose and starch as the polymer framework to which ion-exchange groups are attached. We shall deal in turn with all three methods of synthesis, together with the practical applications of the resulting exchangers.

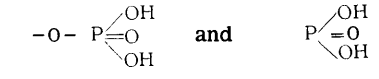
The ordinary universal-ion exchangers have now attained a high degree of reliability. The most flexible methods of synthesis have proved to be those based on styrene polymers, cross-linked with divinylbenzene or with other polyfunctional agents or copolymers of styrene with diolefines[1]. Sulphonation of such polymers gives strong sulphonic acid cation exchangers, while chloromethylation with formaldehyde and HCl gives chloromethylstyrene which combines with tertiary amines to give a strongly basic anion exchanger – a polymeric quaternary base. Chloromethylated polystyrene is a better starting material for the synthesis of resins containing various other functional groups [e.g. the mercapto (SH) group]. Weak cation exchangers – carbolyxic acid resins – are obtained by polymerisation and cross-linking of polymethacrylic acid. A series of anion-exchange resins of intermediate basic strength, containing secondary and tertiary amino groups, are obtained by polycondensation reactions.

These are the better known and generally used ion exchangers. They differ from each other in the dissociation constant of the functional groups, the capacity per millilitre, and the degree of cross-linking or swelling. Their selectivity, although variable, is, in the main, low, the ion-exchange constants not being very different from unity.

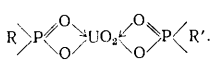
Current problems in the synthesis of selective exchangers call for the introduction of a whole range of different functional groups into polymers. What are the fundamental principles in this field ? The most important body of experience applicable to the development of new sorbents is that of analytical chemistry and the chemistry of complex compounds. In analytical chemistry one of the central principles is the utilisation of sparingly soluble compounds. The same principle applies equally to the development of selective resins. The majority of cations form highly dissociated salts with ordinary sulphonic acid cation exchangers. Ion exchange takes place with equilibrium constants K (i.e. with a change of free energy $\Delta G = -RT\ln K$) that depend on the valency of the ion, its radius, and extent of hydration. When the ion exchange constant is large (several powers of ten), i.e. when the free energy change $\Delta G = -RT\ln K$ is 3000–5000 cal mole^{-1}, sparingly soluble or undissociated compounds are formed between the ion and the resin.

Such compounds are obtained either when the anion-cation bond largely loses its heteropolar nature and becomes covalent or if a coordinate donor-acceptor bond is formed simultaneously with salt formation between the polymer and the cation, i.e. if a chelate compound is formed. Both phenomena can have the same result – a low dissociation constant for the salt – and it is not easy in practice to distinguish between them. Apparently the well-known effect of hydrogen sulphide on the heavy metals is an example of the first. The sulphides of iron, copper, nickel, mercury, etc. are practically undissociated homopolar compounds. The corresponding ion exchangers, containing the mercapto group (SH)[14–17], absorb and hold strongly all the metals of the "H_2S group" – iron, copper, mercury, cadmium, lead, zinc, etc. As in the vast majority of analytical chemical methods, group specificity is encountered here. Cases of absolute specificity for one element are extremely rare.

Fortunately, in problems of practical importance it is not necessary to separate all the elements of the Periodic Table. Usually we are concerned with mixtures of 2–5 components and here a combination of group methods has the desired result. The formation of an internal complex is illustrated by the case of salt formation with the phosphate group[18–20]. Thorium(IV), uranium as the uranyl ion, and iron(III) form weakly dissociated compounds with the phosphoric and phosphonic acid groups,



and



This results in exchange constants for uranium, relative to Ca^{2+}, Cu^{2+}, and Co^{2+}, of about 10^4–10^5. All the rare-earth elements except lanthanum are weakly sorbed on phosphoric and phosphonic acid resins. There are great possibilities here for selectivity and both these types of resin are likely to prove useful.

Before proceeding to a consideration of more complex cases, we shall return to the ordinary ion exchangers mentioned earlier. Of these, a carboxylic acid resin is undoubtedly able to form internal complexes[21–25] and this confers on it a greater selectivity than possessed by a sulphonic acid resin. For example, the exchange constants for Cu^{2+}, Ni^{2+}, and Co^{2+} reach 50–100, relative to Na and K, a fact which cannot be explained by the usual ion-exchange mechanism.

It is interesting that when polymethacrylic acid chain units are diluted with unionised units, i.e. when its capacity is reduced, all its selectivity for the transition metal ions disappears[26]. The reason is the increased distance between the carboxyl groups and consequent impossibility of forming chelates. At present there is little quantitative information about the stability constants of the complex salts formed by polymeric resins. The whole of this field is still in its early stages, but it is already clear that the effects of complex formation with polymeric resins are more pronounced than with low-molecular-weight substances. Here, the particular features of the polymeric framework, carrying the reacting functional groups, are manifested. The change from a dissociated salt to an undissociated one converts the macromolecular polyelectrolyte chains to an uncharged condition, whereupon they coil up in a random fashion; their dimensions become smaller, and the entropy correspondingly increases. In this way complex formation between an ion and the side groups of a linear polymer leads to a more favourable change of free energy than ordinary complex formation with a homologous low-molecular-weight substance. Consequently, the known stability constants of complexes are somewhat greater for polymeric resins, i.e. the polymer stabilises the complex. This is important for the evaluation of the effect of introducing specific complex-forming groups into a resin.

As a first approximation, we can use the stability constants measured for low-molecular-weight ligands, bearing in mind the correction due to the role of the polymer. In recent years a fairly large number of new resins have been synthesised, with various combinations of complexing groups. Most of these are assembled in Table 1, which also indicates their specificity. The most important resins, containing α-hydroxyquinoline group and the ethylenediaminetetraacetate group (EDTA), and most of the others, exhibit group specificity; the stability constants of various metals in the complex, and hence the ion exchange constants, which are their ratios, depend strongly on pH.

Table 2 shows the stability constants of EDTA complexes with various metals (at pH's where dissociation of carboxyl groups is complete).

The equilibrium constant K is given by

$$K = \frac{[MA^{(n-4)+}]}{[M^{n+}][A^{4-}]},$$

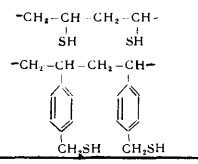
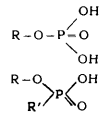
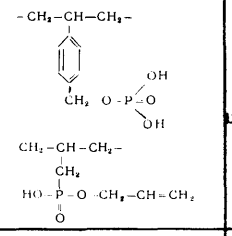
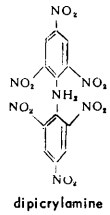
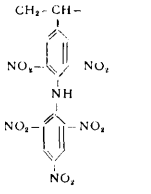
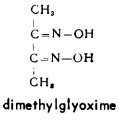
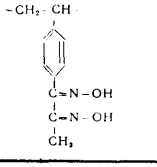
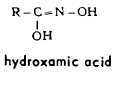
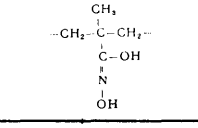
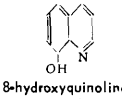
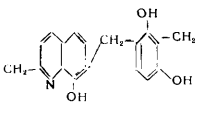
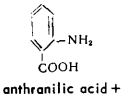
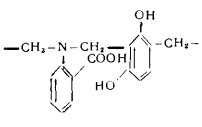
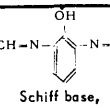
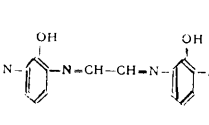
since the ions of metal and ligand combine in equimolar proportions regardless of the valency (n) of the metal. In practice, K is inversely proportional to $[H^n]$ if sorption is carried out at pH < 5, when COOH groups are weakly ionised.

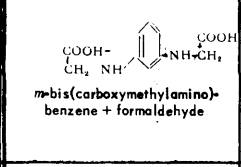
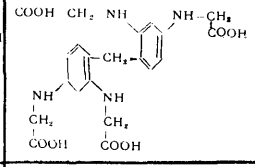
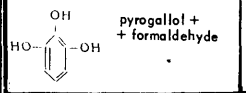
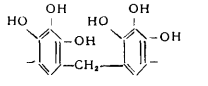
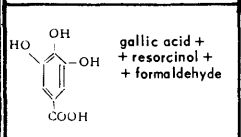
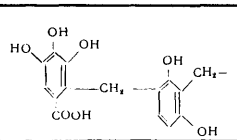
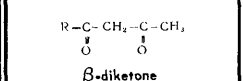
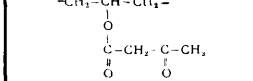
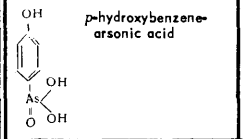
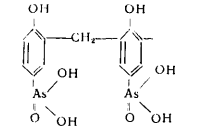
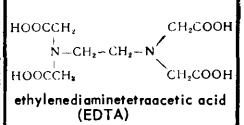
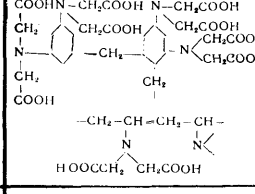
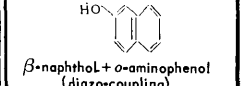
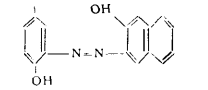
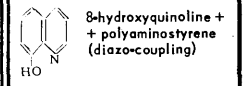
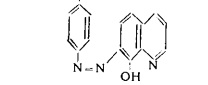
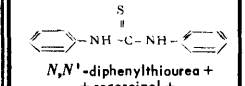
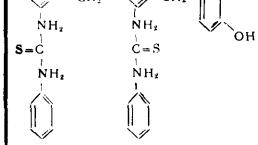
If we absorb a whole group of elements on a specific resin, e.g. the rare earths on a polymeric EDTA, we can elute differentially with solutions of different pH and obtain the individual substances in a pure state. In fact, all the ion-exchange methods now widely used in industry for isolating metals, without exception, make use of complex formation.

It will be recalled that in most industrial plants the extraction of uranium from its ores is accomplished by means of a strongly basic anion exchanger. This utilises the fact that uranium forms the anions $[UO_2(SO_4)_3]^{4-}$ and $[UO_2(CO_3)_3]^{4-}$ in sulphate or carbonate solutions. The same principle applies in the separation of gold as $AuCl_4^-$ from chloride solutions, on an anion exchanger.

The separation of the rare earths is carried out on a large scale on ordinary cation-exchange columns, but with

TABLE 1. Selective and complexing ion exchangers.

Functional group of low-mol.-wt. analogue	Chain structure	Sorption specificity	Reference
R–SH		Ag, Hg^{II}, Fe^{III}, Co, Ni, etc.	14–17
		Th, U^{IV}, UO_2^{II}, Fe^{III}	18–20, 27, 28
 dipicrylamine		separation of K from Na, Ca, and Mg	29–31
 dimethylglyoxime		Ni	32
 hydroxamic acid		Fe^{III}	33
 8-hydroxyquinoline + + resorcinol + + formaldehyde		Cu, Ni, Co	34–37
 anthranilic acid + + resorcinol + + formaldehyde		Cu, Fe^{II}, Zn	36–38
 Schiff base, dinitrophenol + + glyoxal		UO_2^{II}	39

Functional group of low-mol.-wt. analogue	Chain structure	Sorption specificity	Reference
 *m*-bis(carboxymethylamino)-benzene + formaldehyde		Cu^{II}, Fe^{II}, Co^{II}	38
 pyrogallol + + formaldehyde		Hg, Pb, Br	40
 gallic acid + + resorcinol + + formaldehyde		Ca	34, 35
 β-diketone		Cu, Ni, Co	41–43
 *p*-hydroxybenzene-arsonic acid		separation of Th^{IV} from Ca, Mg, and Zn	
 ethylenediaminetetraacetic acid (EDTA)		separation of Cu, Co, and Ni from Na, Ca, and Mg	45, 46
 β-naphthol + *o*-aminophenol (diazo-coupling)		separation of Cu from Na, Ca, and Mg	34, 35
 8-hydroxyquinoline + + polyaminostyrene (diazo-coupling)		Cu, Ni, Co	34, 35
 *N*,*N*'-diphenylthiourea + + resorcinol + + formaldehyde		separation of Cu from Fe^{II}, and Co	

differential elution by complexing substances – citric acid, lactic acid, or EDTA. The difference is that in these traditional methods one makes use of complex formation in the solution while with selective ion exchangers, complex formation takes place on the surface of the exchanger. This has the obvious technological advantage that there is no loss of complexing agent in each elution cycle, which accounted for the main cost of the process and often rendered it uneconomic. Examination of Table 1 shows that complexing resins differ very greatly in their capabilities. A number of resins played an important historical role but are of little interest now, not having especially high ion-

TABLE 2. Stability constants of complexes formed by metal ions with EDTA (in ionic form).

Reaction $M^{n+} + A^{4-} \rightleftharpoons MA^{(n-4)+}$,

$$K = \frac{[MA^{(n-4)+}]}{[M^{n+}]\,[A^{4-}]}.$$

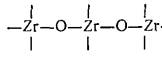
Metal	$\log_{10} K$	Metal	$\log_{10} K$	Metal	$\log_{10} K$
H	10.22	Mn (II)	12.79	Nd	16.61
Na	1.66	Hg (II)	21.80	Sm	17.14
Li	2.79	Fe (II)	14.33	Eu	17.35
Mg	8.69	V (II)	12.70	Gd	17.37
Ca	10.70	V (III)	25.9	Tb	17.93
Sr	8.63	VO	18.77	DY	18.30
Ba	7.76	Fe (III)	25.1	Ho	18.74
Zn	16.50	In	24.95	Er	18.85
Cd	16.46	Ga	20.27	Tm	19.32
Cu	18.80	Al	16.13	Yb	19.51
Ni	18.62	La	15.50	Lu	19
Co (II)	16.31	Ce	15.98	Sc	23.1
Pb	18.04	Pr	16.40	Th	23.2

-exchange constants. Others – for example, the phosphate, sulphydryl, and iminoacetate resins – are very promising.

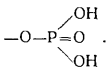
A shortcoming common to many ion exchangers is the strong complex formation with iron, generally regarded as a widespread impurity which must be removed in the separation of rare elements and elements present in low concentration. Another defect of all complex resins is their low chemical stability. Naturally, having spent capital on the synthesis of resins, one must be able to use them for at any rate several hundred cycles. This is frequently not possible, as they gradually lose their functional groups. This circumstance, and also the fact that methods for the synthesis of complexing resins and for their application have been insufficiently developed, explain why the use of such resins has not so far become widespread. However, it must be remembered that the first specimens have appeared only during the last 3–5 years and that the whole of this field is still in a state of flux.

The final choice of one selective resin or another is determined by concrete problems arising in the rare-elements industry. In this connection, several practically important problems, that can be solved by the use of selective complexing ion exchangers, may be mentioned. Among them are the separation of the rare earths on an ion exchanger, of the polymeric EDTA type, separation of the platinum metals, extraction of Ni, Co, Cu, Ag, Au, W, and Mo from diluted residues, possibly using a sulphydryl resin or the EDTA sorbent. Other interesting problems are the extraction of elementary iodine from mineral waters on a polymeric amine[47], and the extraction and purification of certain rare metals used in the semiconductor industry – germanium, gallium, indium, probably as complex anions on anion exchangers. Finally, the sorption of radioactive fission products of heavy nuclei is of great interest.

So far, we have discussed only organic polymeric materials. In recent years it has proved possible to prepare ion exchangers, among them some extremely selective ones, from inorganic polymers based on zirconium, titanium, and molybdenum. It is well known that in solution, zirconium forms chains of the type



Titanium forms similar chains. Polymerisation is particularly marked near the pH's at which the hydroxides are precipitated. If one adds to a solution of zirconium or titanium salt another salt (or acid) with the same or a different anion, at a favourable pH, a zirconyl polymer is precipitated, and the side bonds of the polymer are linked to one or other of the acid residues R. If the acid is polybasic, the anion R, which is firmly attached to the zirconium chain, retains the ability to attach itself to various cations, i.e. we have a cation exchanger. The first cation exchanger to be prepared in this way was zirconium phosphate[48,49]. The R groups attached to the zirconium chain were



The material obtained had the same characteristics as organic phosphate resins. But in contrast to the latter, the inorganic ion exchanger proved to be more stable to heat and to radiation.

The main feature of this material, as of other zirconium sorbents, is the extreme simplicity of preparation, in complete contrast to the complex synthesis of organic resins. In addition to the phosphate cation exchanger (whose capacity was about 1 mg-equiv. g^{-1} at pH 3 and 5 mg-equiv. g^{-1} at pH 11), British workers have prepared a mixed phosphate--citrate cation exchanger, which shows a selectivity towards the rare-earth elements[50]. A whole range of sorbents with zirconium chains carrying various selective functional groups[51] has found application in analysis. These sorbents gave separation factors for certain pairs of ions between 10^3 and 10^4, in one stage. Their properties are summarised in Table 3. Their synthesis is similar to that of the phosphate ion exchanger.

From titanium, phosphate and arsenate ion exchangers have so far been prepared. A new cation exchanger – ammonium phosphomolybdate[52] – is of particular interest for the separation of uranium fission products. Inorganic polymeric sorbents are widening the scope of synthesis of selective ion exchangers and merit detailed study.

TABLE 3. Properties of ion exchangers derived from zirconyl polymers.

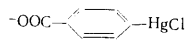
Ion-exchange group	Ions separated	Concentration ratio	Exchange capacity, mg-equiv. g^{-1}
—SH (sulphide)	Cu^{2+}/Ca^{2+}	10^{-3} — 10^{-4}	
	UO_2^{2+}/Ca^{2+}	10^{-3} — 10^{-4}	
	Fe^{3+}/Ca^{2+}	10^{-4}	1.5
$-H_2PO_4$ (phosphate)	Th^{4+}/Ca^{2+}	10^{-4} — 10^{-5}	3
—OOC—CH_2 (citrate) HOOC—C—OH HOOC—CH_2	Ce^{3+}/Ca^{2+}	10^{-2} — 10^{-3}	1.5
	La^{3+}/Ca^{2+}	10^{-2} — 10^{-3}	
$-HC_2O_4$ (oxalate)	Co^{2+}/Ca^{2+}	10^{-3} — 10^{-4}	0.75
	Sr^{2+}/Mg^{2+}	10^{-4} — 10^{-5}	
$-H_2AsO_4$ (arsenate)	Co^{2+}/Ca^{2+}	10^{-5}	1.5
$-HCrO_4$ (chromate)	Sr^{2+}/Ca^{2+}	10^{-4} — 10^{-5}	0.6
$-HCO_3$ (carbonate)	Ca^{2+}/Mg^{2+}	10^{-2} — 10^{-3}	1.2
$-NO_2$ (zirconyl nitrite)	Co^{3+}/Ca^{2+}	10^{-4}	1.5

3. PROBLEMS IN THE PURIFICATION OF ORGANIC SUBSTANCES

The preparation of selective sorbents for absorbing organic substances from the gas or liquid phase deserves special consideration. The technical problems of purifying organic products, e.g. diolefines prior to polymerisation, are very acute at present and require development along new lines. The object is to remove hundredth and thousandth parts per cent of impurities that do not yield to separation or fractional distillation. This field is still in its early stages but its prospects are vast. We shall deal only with a few examples and possibilities. A very simple case is the sorption of different phenols on a sulphonic-phenolic resin in its H form. Here, the principle "like absorbs like" applies [53,54].

Anion exchangers in CN- or bisulphite form are selective sorbents for aldehydes and ketones [55,56]. Polymers containing boric acid groups selectively absorb polyhydric alcohols and carbohydrates [57-59].

Metals that complex with organic ligands were discussed as adsorbates earlier. However, they can equally well serve as adsorbents if it is required to absorb organic substances with characteristic functional groups. Thus, mercury atoms on a sorbent function as traps for mercapto compounds. The sorbents are made in two ways. (1) By the reaction between an alcohol-soluble phenol-formaldehyde resin and mercuric acetate in alcohol solution [60]. The mercury salt of the phenolic groups in the resin is precipitated. (2) Another method of making a "mercury sorbent" is to saturate a strongly basic anion exchanger with *p*-chloromercuribenzoate [61]:



The sorbent obtained is specific for substances containing the SH group; elution may be effected with a solution of H_2S.

Amines are sorbed on cation exchangers saturated with silver or copper ions, since the latter when sorbed on the resin lose none of their ability to complex with organic molecules [62]. It may be predicted that a cation exchanger saturated with cobalt, iron, or copper, and carefully dried, would specifically remove from hydrocarbons substances that can complex with cobalt, etc., such as alcohols, aldehydes, and ketones. Another interesting example is the specific sorption of acetylene on substances of a ketonic nature [63]. Poly(methyl vinyl ketone) might be a suitable sorbent for acetylene. The number of possibilities is immense.

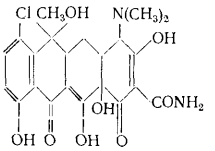
Another practically important question is the use of ion exchangers for purifying large complex organic ions – antibiotics, vitamins, alkaloids, etc. Work with such ions makes special demands on exchangers. Firstly, it seems that the polymer chains must be weakly cross-linked so that the network will be permeable to large ions. In other words, for sorbing large organic ions it is necessary to use strongly swelling exchangers. Thus, a whole range of SBS sulphonic cationites (butadiene-styrene sulphonic acid type) have been synthesised, having different degrees of swelling (swelling coefficients from 1.2 to 6–7). For the sorption of antibiotics mol. wt. 600–800, it is necessary to use a resin with a swelling coefficient of 2.5–3 (with certain antibiotics, the phenomenal quantity of up to 2 g per g of resin can be absorbed) [64,65].

For the sorption of such large ions as insulin (mol. wt. 12 000) a maximum-swelling resin is used (swelling coefficient 5–6). A capacity of 0.3–0.5 g per g of resin can thus be achieved [66].

For the sorption of inorganic ions, strongly cross-linked resins (swelling coefficient 1.2–1.3) are quite suitable. Hence, it is possible to use ion exchangers as molecular sieves, using a strongly cross-linked resin for desalting without loss of the organic ion, or separating a high-molecular-weight protein ion from low-molecular-weight amino-acids and peptides; this has often been done in our laboratory.

A second important factor is the steric impossibility of large ions occupying all the sites on closely spaced functional groups. Thus in an ordinary ion exchanger half or even more of the groups are substituted by ions of low-molecular-weight impurities, which are eluted with the desired product and contaminate it. This gives rise to a unique problem – the making of a strongly swelling exchanger with widely separated ion-exchange groups.

For sorbing streptomycin from a culture liquid, a special resin (KFUKh) was made on this principle. This is the product of simultaneous condensation of phenoxyacetic acid, chlorophenol, and formaldehyde [67]. In this resin, the phenoxyacetic acid units carry carboxyl groups while the chlorophenol units simply increase the distance between them. In the case of large complex ions problems of selectivity are also very acute. Thus, when antibiotics of the tetracycline group, e.g. aureomycin,



are sorbed on swelling sulphonic acid cation exchangers, the exchange constant relative to the Na^+ ion reaches the unusually high value of about 10^3. This indicates that in this case forces other than electrostatic are also acting. Apparently, hydrogen bonds are formed between the hydrogen of the amide group and the sulphonic acid group.

Even more characteristic effects are observed in the sorption of the penicillin anion on anion-exchange resins. It was noticed that the sorption and, more especially, the elution of penicillin were strongly dependent on the simultaneous presence of sulphate and phosphate anions. It was supposed that the additional bonding of the peptide groups of penicillin by means of hydrogen bonds with neighbouring adsorbed sulphate or phosphate created such large additional forces that the penicillin anions would not elute from the surface.

It proved possible to use this circumstance in sorbing penicillin on a sulphonic acid cation exchanger. Penicillin is sorbed on a high capacity resin (200–300 mg per g) as uncharged molecules, held by hydrogen bonds [68]. Elution proceeds well if 10% of acetone or 0.1% of urea are added to the solution of mineral acids; these break the hydrogen bonds formed by the peptide groups. From the infra-red spectra of a thin sulphonic acid cation-exchange membrane, it was shown that the peptide group of penicillin is involved in hydrogen bonding when it impregnates the membrane.

The sorption of an acid such as penicillin on what would seem to be an unnatural sorbent – a cation exchanger – permits the development of a selective method of purification. The purposeful creation (here one can use the term

"construction") of polymeric resins for the selective sorption of complex organic substances is a fairly literal application of the "lock and key" principle. Sorbent and sorbate must correspond to each other in their spatial configuration. The sorbent must contain suitably spaced groups having a given polarity or capable of forming hydrogen bonds with the sorbate. All this leads to a multitude of problems, which we shall not consider in detail.

In conclusion, we shall deal with the ion-exchange sorption of extremely complex substances – proteins and nucleic acids. Here there arises a special difficulty – the possibility of denaturing the material, of altering its macromolecular structure and thereby depriving it of its specific biological activity. The structures of many resins have unfavourable features which are harmful to the proteins being sorbed. Thus, sulphonic acid resins with closely spaced groups can form numerous hydrogen bonds with the peptide groups of a protein and assist the untwisting of its chains, thus destroying its natural spiral structure. In other cases the presence of the hydrophobic hydrocarbon portions in addition to the hydrophilic groups can have an unfavourable effect. For the sorption of these substances, ion exchangers based on cellulose and starch[69] are therefore of particular interest. Among these are the sulphonic acid cation exchangers prepared by the action of $ClCH_2SO_3H$ on cellulose powder, swollen in NaOH. A strongly basic anion exchanger, triethylaminoethylcellulose has been obtained as the bromide salt from diethylaminoethylcellulose and C_2H_5Br. An alternative method of obtaining quaternary bases is by the reaction of cellulose with triethanolamine and epichlorohydrin. Diethylaminoethylcellulose has been prepared from cellulose and 2-chlorotriethylamine. Treatment of an alkali cellulose with monochloroacetic acid gave a carboxylic acid ion exchanger, while treatment with $POCl_3$ gave a phosphate exchanger.

Cellulose ion exchangers, although they have a lower capacity (up to 0.5 mg-equiv. g^{-1}), have found wide application for the fractionation of biologically active proteins, nucleic acids, and viruses[70,71]. In contrast to the resins, this sorbent has proved to be exceptionally reversible and non-denaturing, apparently owing to the homogeneity and hydrophilic nature of its surface and the absence of hydrophobic groups. It is known, for instance, that sugars in enormous concentration not only do not denature proteins but actually improve their stability. The polymer framework of a cellulose sorbent has the same effect.

From the technological aspect, the application of ion exchangers to active protein preparation promises radical changes in the methods of production of serums, vaccines, antibodies, enzymes, and hormone proteins, i.e. the most important medical preparations.

4. POLYMERIC RESINS AS AIDS TO CHEMICAL REACTION

In recent years, a new application of ion exchangers has begun to develop – their use as catalysts in chemical reactions. This field undoubtedly has great possibilities. We have before us the example of nature, where all chemical reactions proceed in extremely mild conditions, with exceptional selectivity and high efficiency. They are all catalysed by enzymes, i.e. by macromolecular protein materials. Enzymic catalysis is undoubtedly associated with a certain combination of closely spaced functional groups, i.e. with the synergism of several groups. In synthetic resins, this principle has never yet been used.

All applications of ion exchangers as catalysts have so far been fairly primitive. Monofunctional polymers have been used to catalyse reactions requiring hydrogen or hydroxide ions. In other words, ion exchangers have been used as acid or basic catalysts. Their advantage is that solutions of acid or alkali, which have subsequently to be removed and which (particularly acids) cause corrosion difficulties with apparatus, need not be added to the reaction mixture. There are numerous examples of syntheses carried out under the influence of ion-exchange materials; some of these have been introduced in large-scale industry.

The simplest applications are in saponification and esterification. A certain element of specificity was found in these cases. Thus, high-molecular-weight esters (polyvinyl acetate) are more difficult to hydrolyse in the presence of ion exchangers, while low-molecular-weight esters react vigorously. Similarly, starch is not hydrolysed by polymeric ion exchangers, although it breaks down under the influence of ordinary mineral acids.

Other examples of specificity arise if some of the hydrogen ions in a sulphonic acid cation-exchange resin (sulphonated polystyrene) are replaced by organic cations – quaternary ammonium bases. Thus, if the quaternary base belongs to the aliphatic series (e.g. cetyltrimethylammonium), the ion exchanger is specifically active for the saponification of aliphatic esters, while if the cation contains aromatic groups (e.g. methyltribenzylammonium), the resin is specific for aromatic esters (methyl phenylacetate).

Nitriles can be hydrolysed in the presence of strongly basic anion-exchange resins, and disaccharides and peptides can be hydrolysed in the presence of sulphonic acid cation exchangers. Condensation reactions that can successfully be brought about by ion-exchange resins include not only esterification but acetal formation and aldol condensation (e.g. the synthesis of pentaerythritol). The latter is particularly successful on weakly basic anion exchangers. The condensation of acetone to mesityl oxide, and of nitroparaffins with aldehydes, can be brought about with strongly basic anion exchangers. All these reactions proceed in mild conditions, between room temperature and 100°. The dehydration of alcohols is another important reaction that occurs on sulphonic acid cation-exchange resins. The production of dioxane from ethylene glycol on sulphonated copolymers of styrene at 150° is an example.

The hydration of unsaturated hydrocarbons is equally successful on sulphonic acid resins. In particular, the Kucherov reaction (hydration of acetylene) can be catalysed by partially saturating a sulphonic acid resin with mercury ions. Additions to double bonds should also be mentioned, e.g. the synthesis of ethylene chlorohydrin, the cyanoethylation reaction (the addition of alcohols to acrylonitrile), etc.

An interesting example of catalysis, developed recently, is the formation of epoxides from olefines and peracids. This reaction can be carried out at 50°, with good yields, on a sulphonated polystyrene catalyst. It is interesting that attempts to accelerate the reaction with strong mineral acids were unsuccessful, because opening of the epoxide ring occurred. Thus, not only can acidic and basic ion exchangers sometimes replace strong acids and alkalis but they can also lead to new products. Some examples of catalysis on ion exchangers are summarised in Table 4.

In conclusion, we shall deal with electron-exchange polymers[72-75], i.e. resins that can undergo reversible oxidation and reduction. Such resins can oxidise organic substances and change the valency state of variable-valency

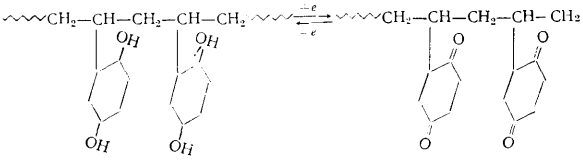
TABLE 4. Examples of catalysis by ion-exchange resins.

Reaction	Equation	Type of resin	t °C	Reference
Saponification of esters	$R_1-\overset{\overset{O}{\|\|}}{C}-O-R_2+H_2O \rightarrow R_1COOH+HOR_2$	sulphonic acid cation exchanger, strongly or weakly basic anion exchanger	35—50	77, 78
Saponification of nitriles	$R-CN+H_2O \rightarrow ROH+HCN$	strongly basic anion exchanger		79
Hydrolysis of carbohydrates	$R_1-O-R_2+H_2O \rightarrow R_1OH+HOR_2$	sulphonic acid cation exchanger		80
Hydrolysis of polypeptides	$R_1-CONH-R_2+H_2O \rightarrow R_1COOH+R_2NH_2$	ditto		81, 82
Esterification	$R_1-COOH+R_2OH \rightarrow R_1-COOR_2+H_2O$	sulphonated polystyrene		83, 84
Acetal formation	$2R_1OH+R_2CHO \rightarrow R_1-\underset{\underset{R_2}{\|}}{OCH}-OR_1+H_2O$		110	85, 86
Dehydration of alcohols	$2HO-(CH_2)_2-OH \rightarrow O\langle \overset{CH_2-CH_2}{CH_2-CH_2} \rangle O+2H_2O$	sulphonic acid resin	150	87
	$C_6H_{11}OH \rightarrow \langle \overset{CH=CH}{CH_2 \quad CH_2-CH_2} \rangle +H_2O$	ditto	150	
Condensation of ketones	$2CH_3COCH_3 \rightarrow \underset{CH_3}{\overset{CH_3}{\diagdown}}C=CH-CO-CH_3+H_2O$	strongly basic anion exchanger		88
Aldol condensation	$2CH_3CHO \rightarrow CH_3-\underset{\underset{OH}{\|}}{CH}-CH_2-\overset{\overset{O}{\|\|}}{C}-H$	strongly basic anion exchanger (quaternary base)	0	89
	$CH_2O+C_2H_5NO_2 \rightarrow CH_3-\underset{\underset{NO_2}{\|}}{CH}-CH_2-OH$		25	90, 91
Additions to double bond	$\underset{CH_3}{\overset{CH_3}{\diagdown}}C=CH_2+H_2O \rightarrow \underset{CH_3}{\overset{CH_3}{\diagdown}}CH-CH_2OH$	sulphonic acid resin	50	90, 91
	$ROH+CH_2=CH-CN \rightarrow RO-CH_2-CH_2-CN$	strongly basic anion exchanger	40	
	$CH_2=CH_2+H_2O+Cl_2 \rightarrow ClCH_2-CH_2OH+HCl$			
Hydration of acetylene	$C_2H_2+H_2O \rightarrow CH_3-CHO$	Hg form of sulphonated polystyrene		93
Epoxide formation	$-\underset{\|}{C}=\underset{\|}{C}-+H_2O_2+CH_3COOH \rightarrow -\underset{\diagdown\,/}{C-C}-+H_2O+CH_3COOH$ (O)	sulphonated polystyrene	40	94

ions by donating or removing electrons from them; transfer of hydrogen ions between resin and solution occurs at the same time. For example,

$$Fe^{3+} + R(red.) \rightleftharpoons Fe^{2+} + R(ox.) + H^+$$

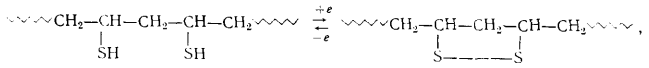
would be a typical reaction. Polyvinylhydroquinone (made by radical polymerisation of the monomer)



and vinylhydroquinone on styrene copolymers were synthesised for use as redox resins. The main difficulty was the insufficient swelling of these resins and the slow diffusion into them. It was overcome by the introduction of hydrophilic groups, for example, by sulphonation of some of the units.

The well-known conversion of hydroquinone to quinone serves as the oxidation-reduction reaction. As usual, the equilibrium of this reaction depends on pH. The polymer can be titrated with an oxidising agent to any redox potential. A supply of such a polymer, brought to a definite degree of oxidation and added to a solution containing variable-valency ions, acts as a redox buffer, i.e. it maintains in the solution a definite ratio between the oxidised and reduced forms. If one uses columns filled with an electron exchanger, one can carry out a complete oxidation or reduction of any form of an ion into another; the total electron exchange capacity reaches 5 mg-equiv. g^{-1}. Polymers, analogous to polyvinylquinone, containing anthraquinone and naphthoquinone, have been synthesised; others have been made by condensation of hydroquinone and its homologues with formaldehyde.

Another class of reversible oxidation-reduction exchangers is that represented by the polyvinylthiol resins:



and the analogous polystyrenethiol resins.

The chief advantage of electron-exchange resins in chemical synthesis is their insolubility and the possibility of carrying out a reaction without contamination by extraneous reagents. In many cases this is very important. For this reason other kinds of electron exchangers which lack this advantage, for example, ordinary cation exchangers saturated with metals of variable valency, do not seem very promising.

The chief drawback of modern electron-exchange resins is the same as that of cation exchangers – inadequate chemical stability, which forbids their use at temperatures that are at all high, and the use of strong oxidising agents for converting them to the oxidised form. For this reason there are not yet any important examples of the industrial application of electron exchangers. All the proposals concerning these materials, – for example, their use as catalysts for oxidations in systems containing an oxidising and a reducing agent at the same time – are very interesting but have not so far been put into practice.

Among the important applications, one should mention the absorption of oxygen dissolved in water on a hydroquinone-pyrogallol condensed resin, which is important in the fight against corrosion, and the preparation of hydrogen peroxide [95].

It is difficult to say at present whether chemical processes using redox resins will prove to be economically profitable. Much depends on the improvement of existing electron exchangers which, as has already been stated, are fairly complex and not very stable.

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THE ANALYTICAL CHEMISTRY OF THALLIUM

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INTRODUCTION

The ever increasing use of rare elements in various technical fields in recent years, and advances in metallurgy, have caused increasing interest in the analysis of such elements as thallium.

The existence of two comparatively stable states (univalent and trivalent) has resulted in a larger number of analytical methods for thallium than for indium and gallium, its analogues. These methods are based on the precipitation of univalent thallium (less often of trivalent thallium), on the oxidation of Tl^+ to Tl^{3+} and the reduction of Tl^{3+} to Tl^+. The Tl^+ and Tl^{3+} ions differ markedly in many of their properties. For example Tl^{3+} shows a pronounced tendency to form complexes, whereas Tl^+ shows practically none. The various complexes which recent studies have revealed, make possible more selective and sensitive analytical methods. A comparatively large number of methods of detection and determination of thallium have been published, but neither the handbook of Fresenius and Jander[1], nor Anderson's survey[2], completely cover the modern methods of analysis of this element.

This review systematises the analytical reactions of uni- and trivalent thallium published in recent years.

1. CLASSIFICATION OF METHODS FOR THE DETERMINATION OF THALLIUM

Detection. Thallium can be detected spectroscopically by a flame test, and by the characteristic formation of crystalline precipitates on addition of potassium iodide, chloroplatinate, chromate[3], thiosulphate[4], iodobismuthate[5], uric acid[6], and picrolonic acid[7], to solutions containing Tl^+, and by the appearance of a characteristic colour when trivalent thallium is treated with benzidine (or *o*-toluidine). The instantaneous oxidation of benzidine by Tl(III) produced from Tl(I) by reaction with Pt(IV), has been suggested as a spot test[8]. A photoluminescent detection of thallium has been described; this is based on the ability of hydrated Tl^+ to luminesce on introduction into the lattice of alkali-metal halides[9]. As little as 0.00012 μg Tl, at a limiting concentration of $1:10^7$, can be detected. The method has been applied to ores and minerals[10]. Reactions accompanied by fluorescence provide the basis for other methods of detection[11,12].

Methods for the determination of thallium. The most accurate methods for determining substantial quantities of thallium are gravimetric, principally involving precipitation as (1) the chromate, Tl_2CrO_4, (2) the iodide, TlI, (3) the thionalidate, $C_{12}H_{10}ONSTl$, (4) the mercaptobenzothiazolate, $C_7H_4NS_2Tl$, (5) the hydroxyquinolinate, $(C_9H_6ON)_3Tl$, (6) the hexamminecobalt(III) hexachlorothallate $[Co(NH_3)_6][TlCl_6]$, (7) the tetraphenylarsonium tetrachlorothallate $[(C_6H_5)_4As][TlCl_4]$, and (8) the diantipyrinylmethane tetrabromothallate, $C_{23}H_{24}O_2N_4.HTlBr_4$.

Of greater practical value are the titrimetric methods in which Tl(I) is oxidised by solutions of $KMnO_4$, $KBrO_3$, KIO_3, KIO_4, or the iodine, liberated when Tl(III) reacts with KI, is reduced with thiosulphate. Potentiometric methods are widely employed, using platinum spirals or discs as electrodes. Determinations of end-points amperometrically or conductimetrically find only slight application, though the former could be developed. A few papers describe coulometric methods based on the oxidation of Tl(I) with electrolytically generated substances such as free halogens or ferricyanide.

In industry thallium is frequently determined polarographically, after extraction from solution

The most important of the spectrophotometric and photometric methods involve precipitation of complex chlorides (or more seldom bromides), TlX_4^-, with large cations of various triphenylmethane dyes. The compounds formed are extracted with solvents such as benzene or toluene, and the optical density of the extracts measured; the dyes themselves remain in aqueous solution. The commonest dyes employed are methyl violet, rhodamine B, brilliant green, and certain other basic dyes.

Spectroscopic methods for determining thallium are most sensitive and widespread in analytical practice. Thallium can be detected by introducing a powder containing it into an oxy-acetylene flame: by the appearance of a green line at 5360.46 Å, 10^{-3}–5.10^{-4}% of thallium can be detected[13]. Spectroscopic methods have been described for determining thallium in zinc[14,15], in cadmium[16,17,18], in lead-zinc ores and the products of their processing[19], in lead[20,21], in soil[22], in pyrite[23], in zinc blende[24], and in ores and minerals[25]. The application of this method in forensic medicine is also described[26].

Traces of thallium may be determined by an activation method[27,28].

The separation of thallium from accompanying elements and its concentration. Extraction of thallium dithizonate at pH 10 from solution containing cyanide and citrate, permits the separation of this element from many others which form stable cyanide and citrate complexes. Extraction with diethyl ether from solutions 4M in HCl or 1M in HBr is most important: in the first instance Fe, Ga, Hg, Sb, Au, and Mo are extracted besides Tl; in the second, a more selective separation is achieved; only Hg, Sb, and Au accompany Tl. Subsequent separation from these elements is effected chemically: Hg and Au are plated out on copper (Sb is only partially removed). Antimony is removed by coprecipitation of small quantities of thallium with ferric hydroxide in the presence of excess alkali[29], or by means of the SBS cation exchanger in the presence of citric, tartaric, or oxalic acids[30], separation from the other elements being also accomplished.

The separation of thallium from many elements, including Hg, Ag, Cu, Cd, Zn, etc., by precipitation as $TlClO_4 . 4CS(NH_2)_2$, has been described.

A good method of concentration and simultaneous separation from accompanying elements consists in coprecipitation with silver iodide,[31,32], with manganese(IV) hydroxide[33], with ferric hydroxide[33a,33b], or with the precipitate formed by *p*-dimethylaminoazobenzene and the sodium salt of *p*-dimethylaminoazobenzene-*p*-sulphonic acid[34]. The mechanism has been studied of the coprecipitation of thallium sulphide with the sulphides of metals of the "H_2S group" in analysis[35,36,37], and with zinc sulphide[37a]. Also coprecipitation with calcium phosphate[38], barium and lead chromates[39], lead sulphate[40], and cuprous and mercurous iodides[40a], have been studied.

2. ANALYTICAL REACTIONS OF THALLIUM (I)

The Tl^+ ion shows some resemblance to Group I cations, Pb^{2+}, Hg_2^{2+}, and Ag^+ ("HCl group" in analysis), and also to the alkali-metal ions K^+, Rb^+, and Cs^+. This dual nature is ascribable to its ionic radius (1.49 Å, cf. K^+ 1.33 Å, Rb^+ 1.49 Å, Cs^+ 1.65 Å) and the value of the electrostatic function z^2/r (Tl^+ 0.67, K^+ 0.75, Rb^+ 0.67, Cs^+ 0.61), the latter indicating a tendency to form typically ionic compounds. Thus Tl^+ forms sparingly soluble compounds with the same anions as the larger alkali-metal cations, and is precipitated by $[Co(NO_2)_6]^{3-}$, $[PtCl_6]^{2-}$, $[BiI_4]^-$, or $[BiI_5]^{2-}$, and $H_4[P(Mo_2O_7)_6]^{3-}$.

On the other hand Tl^+ resembles Ag^+, in that it forms bonds which are largely or completely covalent (characterised by Yatsimirskii[41], in terms of the difference between the ionisation potential of the atom and the heat of hydration of its ion). Thus relatively small ions such as Cl^-, Br^-, and I^-, with easily polarised electron clouds, combine with Tl^+ to give compounds of low solubility, due to the sharp increase in lattice energy brought about by the introduction of covalent links in the crystal. Hence Tl^+ reacts with ions and molecules which tend to form covalent links, such as mercaptobenzothiazole, thionalide, dithizon, thiourea, and Reinecke salt. Thus, many precipitation reactions are known for Tl^+, but few are selective.

A. Precipitation

Precipitation as the chromate. Crookes[42,43,44] observed in 1861, when he discovered thallium, that the addition of K_2CrO_4 to alkaline solutions of Tl^+ gave a yellow precipitate practically insoluble in water. Browning and Hutchings[45] first described the gravimetric determination of thallium as Tl_2CrO_4, without indicating the solution for washing the precipitate. Moser and Brukl[46] determined the solubility of Tl_2CrO_4 in water, alcohol, and solutions of NH_3 and K_2CrO_4. At 20° the solubilities were 8.15×10^{-5} mole/litre in water and 1.14×10^{-5} mole/litre in 96% alcohol: from these results they worked out the following gravimetric method: an ammoniacal solution of Tl^+ is brought to the boil and K_2CrO_4 is added with stirring till there is a 2% excess (the concentration of NH_3 is unspecified). After standing 12 h the precipitate is washed by decantation with 1% K_2CrO_4 solution, then with 50% alcohol till the washings are colourless, and is dried at 120°. Mach and Lepper[47] used 1.25% solutions of NH_3 and K_2CrO_4. Bodner and Terenyi[48] carried out a parallel determination with $KMnO_4$ to verify the precipitation method. Bashilova[49] verified that the optimum concentrations of NH_3 and K_2CrO_4 were 1%. The possible temperature range for drying was found to be 97°–745° by thermogravimetry[50].

Thallium can be determined by the chromate method in the presence of Be, Al, Fe, Cr, Zn, Cd, Ni, Co, Ag, Hg, Cu, if the latter are converted to suitable complexes[46]. The Tl^+ ion mixed with Tl^{3+} can be determined in aqueous $HClO_4$ solution. Another method of precipitation of Tl^+ employs Na_2CrO_4, NaCN, ethanol, and a slight excess of ammonia[51,52]. If the solution contains Fe^{3+} besides Tl^+ and Tl^{3+}, then the alkaline $Fe(CN)_6^{3-}$ oxidises the Tl^+ to Tl^{3+}, and the estimation of Tl^+ is impossible. Forchheimer and Epple[53] suggested the separation of Tl^+ from other ions by precipitation from a 1M $HClO_4$ solution with Na_2CrO_4 solution: Tl^+ is said to be precipitated quantitatively as chromate and dichromate. The precipitate is washed with 1 M NH_3 and 1 M NaCN containing 1 g of Na_2CrO_4 per 150 ml, and weighed as Tl_2CrO_4.

Halide ions, Bi, Pb, Mn, Th, Zr, Ti, Ce, Ga, Sn, and reducing ions interfere with the chromate method. The small selectivity of the method and the high conversion factor to thallium (0.77895) limit its use in analysis. An easier method involves the iodometric back-titration of an excess of added chromate[54]. Amperometric titration of Tl^+ by K_2CrO_4 is possible using a dropping mercury electrode at -0.6 to -0.7 V and Complexone III (EDTA tetrasodium salt) to mask interfering ions[55].

Precipitation as dichromate. Bashilova suggests[56,57] a method of precipitation of Tl^+ from acid or neutral solution by means of excess chromium trioxide. The crystalline precipitate of $Tl_2Cr_2O_7$ (large crystals) is allowed to stand for two hours before filtration and drying at 110°–130°. Fewer ions interfere than in the precipitation as Tl_2CrO_4.

Precipitation as iodide. Though less sensitive than the chromate method, precipitation by KI solution is widely used. Thallous iodide forms a greenish-yellow or orange-yellow finely crystalline precipitate which becomes straw-yellow on standing. The solubility of TlI (2.4×10^{-4} mole/litre) is ten times that of Tl_2CrO_4 (2.41×10^{-5} mole per litre).

The gravimetric estimation of TlI was first elaborated by Lepper[58]. The acetate solution of Tl^+ is warmed to 80°–90°, 4% KI solution is added, the precipitate is cooled, filtered in a crucible, washed with a solution containing 1% KI and 1% CH_3COOH, followed by 80% acetone, and then dried at 120°–130°. The conversion factor to thallium (0.6170) is more favourable than for Tl_2CrO_4. The possible drying range is 70°–473°.[50] The iodide method is recommended for mineral analysis[59,60]. It is sufficiently selective if Complexone III is added to the acetate solution to mask the ions of Pb, Cu, Fe, Bi, etc.[61]. It is used to estimate Tl in metallic lead: if Pb^{2+} is bound with ammonium acetate the limit of detection is 0.4% Tl.[62] Tl^+ may be titrated with standard KI solution using bromophenol blue as adsorption indicator[63,64]. Thallium can be determined by treatment of precipitated TlI with zinc and concentrated HCl, titrating I^- with standard KIO_3 solution[65]. Amperometric[66] and radiometric[67] titrations of Tl^+ with KI solution are possible.

Precipitation with Reinecke salt. A recent method for thallium estimation involves precipitation from acid, neutral, or weakly basic solution with Reinecke salt, $NH_4[Cr(SCN)_4(NH_3)_2]$.[68,69,70] The solubility of the thallium derivative of the salt at 18° was found to be 8.7×10^{-6} mole/litre (using Tl^{204}),[71] and 5.3×10^{-5} mole/litre (by weighing the residue from evaporation of a saturated solution)[72]. The precipitate can be titrated in aqueous HCl in the presence of benzene with KIO_3 solution till the pink colour in benzene disappears; not less than 0.2 mg of Tl in 25 ml may be determined in this way[73]. Alkali, alkaline-earth and "sulphide group" (in analysis) cations do not interfere with the determination. This method is preferable to those described previously (smaller solubility and conversion factor to Tl).

Precipitation as iodate. Rao[74] describes the precipitation of $TlIO_3$, but as the solubility is 1.85×10^{-3} mole/litre, the method has little use.

Precipitation as cobaltinitrite. This method[75] gives a precipitate whose composition is independent of Tl concentration and corresponds to $Tl_3[Co(NO_2)_6]$.[76] Prolonged action of the reagent leads to a change in composition of the precipitate, introducing some $Tl_2Na[Co(NO_2)_6]$. The solubility of $Tl_3[Co(NO_2)_6]$ determined using Co^{60} and Cs^{134}, was 8×10^{-5} mole/litre at 20°.[77] In the presence of silver, thallium forms a precipitate of $Tl_2Ag[Co(NO_2)_6]$ which is easily soluble in aqueous-acetone NH_4SCN solution; the Co^{2+} in solution is then equivalent in quantity to the thallium and is titrated with Complexone III solution till the blue of the cobalt thiocyanate disappear[78].

Precipitation as mixed ferrocyanides. Thallium resembles Rb^+ and Cs^+ in forming mixed ferrocyanides. Tananaev and Glushkova showed[79] that thallium forms sparingly soluble ferrocyanides with magnesium, calcium, and strontium, of composition $Tl_2M[Fe(CN)_6]$, as well as $Tl_2Cu_3[Fe(CN)_6]_2$, $Tl_4Ni_4[Fe(CN)_6]_3$, $TlLa[Fe(CN)_6].4H_2O$, $TlCe[Fe(CN)_6].3H_2O$, $Tl_2(UO_2)_3[Fe(CN)_6]_2$, and $Tl_4(UO_2)_4[Fe(CN)_6]_3$. Ssuspensions of copper, nickel, and uranyl ferrocyanides can evidently be used to remove traces of thallium. Potentiometric titrations with $K_4Fe(CN)_6$ in the presence of calcium ions with an electrode reversible with respect to the ferri–ferrocyanide system[80] and conductimetirc titrations[81], have been suggested.

Precipitation as sulphide. This is inaccurate because the precipitate tends to adsorb other materials and to oxidise in air. Small quantities of thallium, however, can be titrated radiometrically, using a solution of Na_2S containing S^{35},[82] or photometrically[83].

Other inorganic precipitations. The reaction of Tl^+ with $Na_2S_2O_4$[84,85] has been used to determine Tl nephelometrically. Conductimetric titrations of Tl^+ with KSeCN[86] and KSCN[87] are also possible.

Precipitation with organic reagents. The use of organic reagents enables Tl^+ to be determined with greater sensitivity, and occasionally with greater selectivity. Thallium tetraphenylboron has a solubility of 6×10^{-7} mole/litre (found radiometrically)[88], and the sensitivity of the precipitation is 9 μg Tl/ml. Wendlandt[89] elaborated a gravimetric method using sodium tetraphenylboron; the precipitate is dried at 100°–105°; Tl^+ is also titrated conductimetrically using this reagent[90]. Radiometric titration has been applied to various technical products[91].

Most characteristic of Tl^+ are precipitations with reagents containing -SH and >C=S groups. Precipitation with mercaptobenzothiazole[92], or thionalide[93,94], in alkaline tartrate–cyanide solution permits the separation of Tl^+ from all major impurity elements. The microgravimetric determination with thionalide is performed as follows: 0.5 ml of 10% CH_3COONa, 0.25 ml of 20% KCN, and 0.5 ml of 2*N* NaOH are added, and then, to the solution at 80°, containing 3–6 mg Tl^+, are added 25–35 ml of thionalide in acetone. The precipitate is dried at 110°.

Sodium diethyldithiocarbamate and other dithiocarbamates[95-98] form sparingly soluble internal complexes with Tl^+. Dithizon forms a compound with Tl^+, with a dissociation constant $K = 4.35 \times 10^{-6}$,[99] which is stable enough for its use in the quantitative extraction of Tl^+ from elements which interfere with its spectrophotometric determination[100-102].

Other precipitations use 3-mercapto-4-hydroxytoluene[103], the β-semicarbazones of isatin and *N*-benzylisatin[104], the thioderivative of salicylaldehyde[105], 8-mercaptoquinoline[106], thioacetamide[107], *o*-mercaptoacetamido-*p*-nitrophenol[108], and *p*-(mercaptoacetamido)acetanilide[109].

B. Oxidation

The normal redox potential of the couple Tl^{3+}/Tl^+ is 1.222 V in *N* H_2SO_4.[110] The thallous ion reduces silicomolybdic acid to the blue form, and can thus be determined photometrically in solutions of 0.7–0.4 mg Tl^+/10 ml.[60]

In acid solution containing sufficient Cl^- to complex Tl^{3+} firmly, Tl^+ reduces $KMnO_4$ to Mn^{2+},[111-113] and in alkaline medium to MnO_2 or to K_2MnO_4 in the presence of $BaCl_2$.[114,115]. Thallous ion is used to back-titrate the excess $KMnO_4$ after oxidation of H_2O_2 and hydrazine[116], and in the course of the estimation of Pb^{2+}, Se^{4+}, Te^{4+}, and Cr^{3+}.[117] Salts of Tl^+ selectively reduce MnO_4^- in the presence of $Cr_2O_7^{2-}$;[118] Tl^+ can be titrated with $KMnO_4$ in the presence of KBr and the indicators victoria ruby-red, acid black 10B, methyl orange, and indigocarmine[119].

Desmukh[120] suggested iodine in alkaline solution as an oxidant of Tl^+, excess iodine being titrated with thiosulphate. He also used selenious acid which was reduced by Tl^+ to elementary selenium[121].

The thallous ion in 28–37% HCl solution reduces IO_4^- [122] and $K_7Cu(IO_6)_2$ [123] to ICl.

It also reduces other oxygen containing oxidants such as KIO_3 and $KBrO_3$: Tl^+ can be titrated with KIO_3 in the presence of KI, [124] and of HCl. [125] The following titrations of Tl^+ have been described: with chloramine-T in HCl solution with indigosulphonic acid as indicator [125]; with Ce^{4+} and ferroin; [126] and with vanadate in the presence of ICl as catalyst [127]. Potentiometric titration with $KBrO_3$ in acid solution can be carried out in the presence of Na_2HPO_4 which complexes Fe^{3+}. [128]

In alkaline solution Tl^+ is titrated potentiometrically with $K_3Fe(CN)_6$. [129,130] Tl^+ is oxidised with chlorine or bromine water [131] (excess chlorine is removed by boiling, and excess bromine by reaction with phenol or sulphosalicyclic acid), and with potassium or ammonium persulphate in solutions containing about 1 M free H_2SO_4.

Thallous ion has been titrated coulometrically with $Fe(CN)_6^{3-}$, [130] Cl_2 or Br, [131] generated electrolytically, the end-point being found potentiometrically or amperometrically.

The Tl^+ ion is oxidised at a rotating platinum electrode [132,133], at which half-wave potentials become more positive with lower pH values.

The Tl^+ ion is quantitatively deposited as Tl_2O_3 by electrolytic oxidation under defined conditions, but the method lacks sufficient accuracy [134]. Thallium separates quantitatively at the anode from ammoniacal NH_4NO_3 solution if the solution contains Cu^{2+} as a depolariser preventing deposition of thallium at the cathode [135]. Thallium separates from metallic cadmium by electrolysis in ammoniacal solution at 2 V potential and 0.2–0.4 A current [136]. Internal electrolysis with a Pb/PbO_2 cathode in sulphuric acid at pH 1.5, causes thallium to separate quantitatively as Tl_2O_3, even in the presence of 100-fold excess of Ag, Cd, or Zn. [137]

C. Reduction to the Metal

Polarographic reduction at a dropping mercury electrode. The half-wave potentials depend relatively little on the nature of the supporting electrolyte in the reduction of Tl^+ to the metal [138]. The Tl^+ ion has featured in many studies of the influence of ionic strength on the magnitude of diffusion current [139], and in the determination of diffusion coefficients in solutions of various electrolytes [140]. Recently the polarographic constants of thallium (I_d, $E_{\frac{1}{2}}$, D) have been published for various non-aqueous media: ethylene glycol [141], ethylenediamine [142], formamide [143], mixtures of formamide and acetamide [144], aqueous-alcoholic solutions of indifferent electrolytes [145], absolute ethanol [146], and aqueous dioxan [147].

Aqueous solutions are widely employed for the polarography of thallium, used successfully in the determination of thallium in highly purified zinc [148], and in lead [149], cadmium [150,151,152], indium [153], and zinc salts in the presence of tin [154].

Electrolytic reduction at other electrodes. Thallium is deposited at a cathode as a weakly adhering mass which is easily oxidised in air [134]: it is deposited at a mercury cathode from a solution containing nitric and benzoic acids [155]. The results obtained are somewhat high; the maximum error of 6.25% is probably due to oxidation of the thallium. Electrolytic deposition of Tl^{204} from $Tl^{204}ClO_4$ solution has been described [156].

D. Complex Formation

The Tl^+ ion, like Ag^+, forms rather unstable complexes with halide ions, which have been studied spectrophotometrically [157] and their solubilities have been determined. The former study showed the existence in solution of undissociated molecules TlCl and TlBr, and that on addition of excess halide ions new absorption peaks appear nearer the infra-red region, due to TlX_2^-, TlX_3^{2-}, TlX_4^{3-}. Determinations of thallium based on the TlCl peak at 245 mμ (in the presence of lead and bismuth) [158], and the fluorescence of $TlCl_3^{2-}$ at 2537 Å, [159] have been described. Kuo-Hao Hu and Scott [160] measured the solubility of TlCl in solutions of alkali-metal chlorides and showed that the $TlCl_2^-$ ion exists and has a dissociation constant of 0.68; they confirmed their results spectrophotometrically [161]. Dissociation constants derived from solubility measurements have been obtained for $TlBr_2^-$, $TlBr_3^{2-}$, [162] TlI_2^-, TlI_3^{2-}, and TlI_4^{3-}. [163]

Thiocyanate complexes, still less stable than the halide complexes, have been studied potentiometrically and from their solubility [164,165]. Thiosulphate complexes have been studied [166]; the dissociation constants of the compounds $Na[Tl(S_2O_3)]$ and $K[Tl(S_2O_3)]$ have been found to be of the order of 10^{-2}. [167] The existence of $Na[Tl(S_2O_3)]$ has been shown polarographically: it has a pK of 1.91. [168]

Complex formation with Tl^+ has been proved for histamine [169], pyrophosphate [170], and citrate [171].

Typical of Tl^+ are the thiourea complexes which may be precipitated with heavy anions such as perchlorate, picrate, and tetrathiocyanatodiamminechromate(III) (from the Reinecke salt) [172]. The presence of Tl^+ is reliably detected by the formation of needle-shaped crystals of $\{Tl[SC(NH_2)_2]_4\}ClO_4$, [173] which also allows the quantitative separation of Tl from impurity elements [174].

The Tl^+ ion complexes with ethylenediaminetetracetic acid only at high pH values [175], making determination difficult by this means. Spectrophotometric titration with a solution of the tetrasodium salt of EDTA (Complexone III) at pH 10 and 222 mμ has been described [176]. The considerable instability of these thallium complexes is shown by the results of high-frequency titrations of equivalent quantities of Tl^+ and the acid with NaOH solution [177]. The dissociation-constant exponents (pK's) of Tl^+ complexes with nitrilotriacetic and ethylenediaminetetraacetic acid at 25° are 3.44 (μ = 1.4) and 5.81 (μ = 1.0), where μ is the ionic strength [178].

3. ANALYTICAL REACTIONS OF THALLIUM (III)

The thallium(III) ion shows pronounced oxidative properties and a tendency to complex with both inorganic and organic ligands. The stability of trivalent ion complexes decreases in the series Tl > Bi > Sb > Fe > Cr > Al. [179]

A. Complex Formation

Hydroxo complexes. Trivalent thallium gives the sparingly soluble hydroxide by hydrolysis even in acid solution. The light-absorption maximum for $Tl(ClO_4)_3$ solution increases as the $HClO_4$ concentration decreases, due to $Tl(OH)^{2+}$ and $Tl(OH)_2^+$ formation, only mononuclear complexes being formed [180]. The pK for the first step of the

hydrolysis is 0.2; [181] at acid strengths from 0.5 to 2.0 M the basic $Tl(OH)^{2+}$ ion is absent from solution. Biedermann [182], in a potentiometric study of the hydrolysis, found

$$K_1 = \frac{[Tl(OH)^{2+}][H^-]}{[Tl^{3+}]} = 7.3\times10^{-2} \text{ and } K_2 = \frac{[Tl(OH)_2^+][H^+]^2}{[Tl^{3+}]} = 2.3\times10^{-3}.$$

The solubility product of $Tl(OH)_3$ at 25° has been reported as $10^{-43.6}$, [181] $10^{-43.8}$, [183] and $10^{-45\pm0.2}$. [184]

Starik [185], studying the state of thallium at a concentration 10^{-4} M in sulphate solutions at various pH values, showed that although at pH 3 trivalent thallium was completely colloidal, it was almost instantaneously coagulated, from which he concluded that thallium hydroxide does not form a stable positively charged colloid. Coagulation ceases at pH 7, above which a fairly stable negatively charged colloid is formed. Thallium may be determined spectrophotometrically [186] as $Tl(OH)_3$ stabilised by the addition of gelatine.

Thallic salts may be used as acid-base titration indicators on account of their easy hydrolysis [187] – for example the Tl^{3+}/Tl^+ system in the presence of KI. [188]

Nitrato complexes. The redox potential for the Tl^{3+}/Tl^+ system is lower in nitric acid than in perchloric acid solution of the same concentration; in 1 M $HClO_4$ the potential is 1.260 V, [183] in 1 M HNO_3, 1.230 V. [189] More recent studies on the rate of exchange between $Tl^{204}ClO_4$ and $Tl(ClO_4)_3$ in the presence of NO_3^- (more rapid exchange) indicate complex formation of Tl^{3+} with NO_3^-. [52] Peshanski [190] found the equilibrium constant to be 1.5 at 18° and μ = 3.5 by a spectrophotometric method. Burns and Whiteker [191] showed that as μ varied from 0.57 to 3.0, the equilibrium constant changed from 8.3 to 2.0.

Sulphato complexes. The lowering of the redox potential of Tl^{3+}/Tl^+ in sulphuric acid solution [192] indicates complex formation of Tl^{3+} with SO_4^{2-} comparable to that with NO_3^-, but the sulphato complexes have been little studied. The magnitude of the solubility product can, however, be found from measurements of hydrolysis in sulphuric acid solution. The values 10^{-38}, [185] and 10^{-37}, [193] are higher than those found from hydrolysis in perchlorate solutions, which confirms the complexing of Tl^{3+} by SO_4^{2-}.

Cyano complexes. The increase in the rate of isotopic exchange in the Tl^+–Tl^{3+} system in the presence of CN^- indicates the formation of $Tl(CN)^{2+}$, $Tl(CN)_2^+$, and $Tl(CN)_3$. [194]

Halogeno complexes. Most fully studied are the chloro and bromo complexes, first demonstrated by the redox measurements of Spenser and Abegg [195] on Tl^{3+}/Tl^+ in the presence of halide ions, and confirmed by Hughes and Garner [196]. Recently chloro complexes have been studied by isotopic exchange between $TlClO_4$ and $Tl(ClO_4)_3$. [197] Benoit [181] found potentiometrically at 25° and μ = 0.1–0.2 pK values (dissociation constant exponents) for the following complexes: $TlCl^{2+}$ (pK_1 = 8.1), $TlCl_2^+$ (pK_2 = 5.5) $TlCl_3$ (pK_3 = 2.2), $TlCl_4^-$ (pK_4 = 2.6), $TlBr^{2+}$ (pK_1 = 9.7), $TlBr_2^+$ (pK_2 = 6.9), $TlBr_3$ (pK_3 = 4.6), and $TlBr_4^-$ (pK_4 = 2.7). Peshanski and Valladas-Dubois found the following values for chloro complexes: pK_1 = 6.25, pK_2 = 5.15, pK_3 = 3.10, pK_4 = 2.5, pK_5 = 1.80 (for $TlCl_5^{2-}$); and for the bromo complexes: pK_1 = 8.9, pK_2 = 7.5, pK_3 = 5.7, pK_4 = 4.0, pK_5 = 3.1 (for $TlBr_5^{2-}$), and pK_6 = 2.4 (for $TlBr_6^{3-}$). [157,198] The Tl^{3+}–I^- system is complicated by simultaneous complex formation and oxidation-reduction [198a]. Iodination of TlI in methanol and dioxan gives TlI_3 together with its complexes with dioxan [199].

Sharpe has shown that in aqueous solutions containing KI and TlI_3, TlI_4^- is formed [200], which has been confirmed spectrophotometrically for solutions of I^- and Tl^{3+} in various molar ratios [201]. The pK of TlI_4^- is 32.15. [202]

Halogeno complexes have considerable stability and are widely used in the estimation of thallium: they may be precipitated by organic and inorganic cations of high molecular weight or extracted by organic solvents from complex mixtures.

Of the acid complexes of $HTlCl_4$, but not H_2TlCl_5, is extracted by diethyl ether from solutions containing HCl; [203] by this means thallium is estimated in lead [204], in toxic materials [205], in urine and hair [206], and in certain other cases [207]. Thallium may be separated from all elements except Au and Hg by paper chromatography of its chloro complexes in butanol saturated with 1 N HCl. [208,209,210].

The extraction of thallium from solutions containing HBr was introduced by Wada and Ischii [211], has been studied repeatedly by many workers [212,213,214], and has been employed to estimate thallium in tin–cadmium alloys [215], and in ores and process products of non-ferrous metals [151]. The extraction of thallium from solutions containing HI has been studied but not applied [212,213,214].

Meyer [216] and Renz [217] describe the precipitation of chloro thallium complexes with various organic nitrogenous bases. Bivalent metal chlorides have been used similarly [218]. Thallium may be determined gravimetrically by precipitation as $[(C_6H_5)_4As][TlCl_4]$, though MnO_4^-, IO_4^-, ClO_4^-, SCN^-, NO_3^-, I^-, Br^-, and ReO_4^- interfere [219]. $(C_6H_5)_4AsCl$ and $(C_6H_5)_4SbCl$ are used as precipitants [220]. A finely crystalline precipitate, $[Co(NH_3)_6]TlCl_6$, insoluble in HCl, ethanol, and ether, is formed from $[Co(NH_3)_6]Cl_3$ and a solution containing Tl^{3+} and excess Cl^-. This is used to determine thallium gravimetrically in pure salts and lead alloys [221], and radiometrically using Tl^{204} or Co^{60}. [222,223]. Other complex cation precipitates include $[Co(en)_3][TlCl_6]$, $[Co(en)_2Cl_2][TlCl_4]$, and $[Co(en)_2(NO_2)_2]H_2[TlCl_6]$. [224]

Precipitations involving bromide instead of chloride ions are distinctly more sensitive. The detection of Tl^{3+} as a finely crystalline bromo complex with urotropine and acridine has been described [225]. Sandri [226] used $HTlBr_4$ to detect pyridine, α-picoline, quinoline, urotropine, choline, betaine, caffeine, theobromine, theophylline, and nicotinamide. Busev and Tiptsova [227] studied precipitation of complex bromides with derivatives of pyrazolone, and determined Tl^{3+} gravimetrically using diantipyrinylmethane [227,227a] and spectrophotometrically using the same reagent and diantipyrinylpropylmethane [227b].

Complex iodothallates may be employed analytically, for example thallium may be detected by precipitation as the iodothallates of cocaine, strychnine, codeine, pilocarpine, atropine [228], quinoline [229], pyridine [225], and caesium [230].

The colourless chloro and bromo complexes of thallium precipitated with certain cationic dyestuffs may be extracted by non-polar organic solvents, and the thallium can be estimated by spectrophotometric measurement of the dye-

stuff extract; methyl violet (crystal violet) is commonly used[231-238]. The molar extinction coefficient of the extract of the complex is 48000 at 570 mμ and 64000 at 620 mμ; [234] the optimum acidity is 1 *N* HCl according to Gur'ev, and 0.08–0.2 *N* HCl according to Shchemeleva; excess oxidising agents destroy the dye and should be excluded. Beer's law is obeyed for concentrations of Tl^{3+} from 0.2 to 2.5 μg/ml. [231]

Trivalent thallium is estimated as $TlCl_4^-$ or $TlBr_4^-$ complexes with Rhodamine B; [239,240] the molar extinction coefficient is 87000 at 560 mμ, and the extract fluoresces at 580 mμ. Brilliant green gives a maximum optical density with solutions 0.08–0.16 *N* in HBr, the molar extinction coefficient being 70000. [241-243] Tetramethyldiaminodiphenylantipyrinylcarbinol is used as a precipitant for $TlCl_4^-$; [244] the molar extinction coefficient is 68000 at 638 mμ, Beer's law being obeyed for Tl^{3+} concentrations from 0.1 to 2.0 μg/ml. Certain other dyes have been employed[245]. All spectrophotometric methods based on this principle require previous separation of thallium from Au, Hg, and Sb.

Acetato complexes of thallium are quite stable. Moeller and King showed that in the presence of excess sodium acetate at pH 4.5 Tl^{3+} can be separated from Fe^{3+} as an acetato complex[246]. Toropova found the dissociation constants of $Tl(CH_3COO)_2^+$ and $Tl(CH_3COO)_3$ to be 3.1×10^{-12} and 5.6×10^{-16}, by measuring the redox potential of Tl^{3+}/Tl^+ in the presence of acetate ions[247]. Oxalic acid reduces Tl^{3+} to Tl^+. [247]

Tartrato complexes. The stability of tartrato complexes of thallium(III) relative to those of gallium, indium, and aluminium has been studied[248].

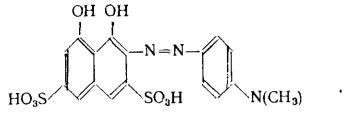
Complexes with amines. 2,2'-Dipyridyl yields $[Tl(dp)_2](NO_3)_3$, $[Tl(dp)_3](NO_3)_3$, and $[Tl(dp)_2](ClO_4)_3$. The dissociation constant of $[Tl(dp)_3]^{3+}$ was found potentiometrically to be $5 \pm 2.5 \times 10^{-26}$. [249] Mixed complexes have been obtained from halide ions and ammonia[250], ethylenediamine, 2,2'-dipyridyl and *o*-phenanthroline[251].

Ethylenediaminetetraacetic acid complexes. Like all trivalent metals, thallium forms an acid-stable compound with Complexone III, which is used for the amperometric titration of thallium at pH 1.0–1.2, in which Tl^{3+} is reduced at a rotating platinum electrode[252]. Flaschka determined thallium by means of EDTA tetrasodium salt, the thallium derivative being more stable in alkali than that of magnesium[253]. Trivalent thallium can be titrated directly against 1-(2-pyridylazo)-napththol with xylenol orange as indicator[254]. In indirect determinations the excess EDTA tetrasodium salt may be back-titrated with zinc salts and benzidine-ferrocyanide as indicator[255], thorium salts and alizarin S[176], ferric salts and sulphosalicylic acid[256], vanadium salts and diphenylcarbazide or diphenylcarbazone[257], cobalt salts and thiocyanate[258]; zinc salts are used for the potentiometric titration of the excess Complexone using a mercury test electrode[259].

Complexes with 8-hydroxyquinoline and its derivatives. Thallic ion precipitates quantitatively with 8-hydroxyquinoline; the precipitate is dried at 120° and weighed as a monohydrate[260,261]. The absorption curve of the chloroform solution shows a maximum at 400–402 mμ, with a molar extinction coefficient of 6790; 1.2–5 μg Tl/ml may thus be determined, though the solution decomposes on ultra-violet irradiation[261]. The solubility product of the 8-hydroxyquinoline complex is 4×10^{-33}. [262] Thallium is precipitated by dibromohydroxyquinoline[260], 2-methyl-8-hydroxyquinoline and 5-nitroso-8-hydroxyquinoline[263]. The 8-hydroxyquinoline[264] and 5-methyl-8-hydroxyquinoline[265] derivatives have been studied thermogravimetrically.

Complexes with various dithiocarbamates. Thallium(III) precipitates quantitatively with diethyldithiocarbamate[95]; the complex is extracted with CCl_4, the extract having an absorption maximum at 426 mμ with a molar extinction coefficient of 1330. Moderate quantities of thallium (600 μg/25 ml) may thus be determined spectrophotometrically: Tl^{3+} is also precipitated by other disubstituted dithiocarbamates[98,266]. The Tl^{3+} ion can be radiometrically titrated with sodium 5-methylpyrazoline-1-dithiocarboxylate[266]. Successive radiometric titration of Tl(III)-In(III) and Tl(III)-Zn(II) can be carried out with 3-methyl-5-phenylpyrazoline-1-carboxylic acid.

Complexes with other organic reagents. Various internal xanthate complexes have been obtained $[Tl(ROCS_2)_3]$ where R = methyl, ethyl, isopropyl, n-butyl, s-hexyl [267]. Certain chromotropic azo-dyes have been studied as reagents for Tl^{3+}, the most sensitive being



with which 0.05 μg Tl(III)/ml can be detected[268]. Evidence exists for thallium complexes with nitrosophenylhydroxylamine and 1-nitrosonaphthylhydroxylamine[269].

B. Reduction

When Tl^{3+} is reduced with KI, the iodine liberated is titrated with thiosulphate[270,271]. Photometric determination of a starch–iodine complex may also be employed[272,273]. The semimicro-determination of Tl^{3+} is carried out by titration in H_2SO_4 with standard KI and a starch indicator[201].

Thallium(III) is determined by photometric measurement of the colour produced by oxidation of certain organic compounds with thallium(III). Thus thallium(III) with *p*-phenetidine at pH 3.1 [274] and with pyramidon gives a reddish-violet colour with an absorption band between 350 and 540 mμ; the solutions obtained obey Beer's law for thallium concentrations between 0.05 and 5 mg per 50 ml, Pb, Bi, Zn, and Cd not interfering[275]. At concentrations up to 0.5 mg/ml Fe(III), Zn, Cd, As, and Cu do not interfere with the determination based on the violet colour obtained with *p*-aminophenol sulphate[276]. With benzidine thallium(III) gives a blue colour, the stability of which depends on the pH of the solution[277]. Electrochemical reduction has been little studied. Smith and Nelson[278] studied the effect of thallium(III) on a dropping mercury electrode in chloride solutions; Hughes and Husch[279] studied the effect in perchlorate solutions, but their results are seldom applied due to the proximity of the redox potential of Tl^{3+} and the anodic-dissolution potential of mercury. Reduction on platinum is of greater analytical use; Songina observed the reversible redox wave for the Tl^{3+}–Tl^+ system using a rotating platinum electrode[280].

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A considerable number of methods for the determination of thallium are based on Tl^{+}, principally involving its precipitation. Insufficient attention has so far been paid to analyses based on reactions of Tl^{3+}. Such reactions, particularly those involving complex formation, are very promising for the development of new methods which may overcome some of the existing inadequacies in the estimation of thallium. Research into thallium(III) complexes should lead to analytical methods satisfying present requirements as regards simplicity, speed, precision, selectivity, and sensitivity.

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VINYLACETYLENE AND ITS HOMOLOGUES

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INTRODUCTION

Vinylacetylene production is one of the main applications of acetylene in present-day industry. The prospects for increased production of vinylacetylene as well as of its homologues were recently greatly improved by the treatment of natural, petroleum and by-product gases. The possibilities for the utilisation of vinylacetylenic hydrocarbons in chemical industry are far from being exhausted, as is

borne out by the number of papers on enynes appearing in recent chemical literature.

Vinylacetylenic hydrocarbons are of considerable interest also for theoretical organic chemistry. Their polarity, high polarisability, and the characteristic rigidity of configuration bring out clearly the influence of structural factors on chemical reactivity.

The chemical literature contains no complete review of the methods of preparation or the properties of enyne hydrocarbons.

Enynes – hydrocarbons with two different types of multiple bonds, double and triple – were little known till about 1930. They began to attract attention after Nieuwland's discovery of the dimerisation of acetylene in the presence of cuprous chloride (1931)[1], which subsequently became a basis for the industrial preparation of chloroprene rubber.

The first enyne hydrocarbons to be prepared were hex-1-en-5-yne (1878)[2] and pent-1-en-3-yne, "perylene" (1882)[3], but the structure of the latter was not established till 1942[4-8]. The first member of the enyne series, vinylacetylene, was described in 1913 by Willstätter[9]. By 1931, besides the above-mentioned hydrocarbons, isopropenyl-[10], isobutenyl-[11], isopentenyl-[12], and allylacetylene[13] had also become known, as had some aromatic vinylacetylenes[14-16]. But the great majority of enyne hydrocarbons known at present, whose formulae and constants are given in Table 2, were first described within the last 20 years, namely after the discovery of the practical value of vinylacetylene.

I. METHODS FOR THE PREPARATION OF ENYNE HYDROCARBONS

Some vinylacetylenes occur in essential oils. For instance, the essential oil from *Agropyrum repens* and some other grasses contains the hydrocarbon "agropyrene" or "capillene", whose structure is apparently similar to, but not identical with, that of phenylpent-2-en-4-yne[17-19].

Enyne hydrocarbons can be prepared by a large number of synthetic methods, acetylene being the most widely used starting material. These are reviewed below in accordance with the nature of the chemical processes involved.

A. PREPARATION FROM COMPOUNDS WITH THE SAME NUMBER OF CARBON ATOMS

1. Preparation from Halogen Derivatives

Dehydrohalogenation of halogen derivatives is a classical method for the synthesis of a very wide range of unsaturated compounds, including the enyne hydrocarbons with conjugated and isolated multiple bonds.

Thus, a series of enyne hydrocarbons was prepared by one of the oldest methods – treatment with KOH of products from the reaction between unsaturated ketones and PCl_5, [2,7,8,20-22]:

$$CH_3-CO-CH_2-CH_2-CH=CH_2 \xrightarrow{PCl_5} CH_2=CCl-CH_2-CH_2-CH=CH_2 \xrightarrow{KOH} HC\equiv C-CH_2-CH_2-CH=CH_2.$$

Hydrogen halides are more easily removed from the halogen derivatives of dienes containing a -CH = CHCl [23,24] group, yielding enynes.

Isomerisation of multiple bonds sometimes occurs during the preparation of enynes from conjugated chlorodienes. Thus, the treatment of 2-chloropenta-1,3-diene with alkali yields vinylmethylacetylene[20,22], instead of the expected propenylacetylene:

$$CH_2=CCl-CH=CH-CH_3 \xrightarrow{KOH} CH_2=CH-C\equiv C-CH_3.$$

Migration of multiple bonds is also observed on dehalogenating allenic chlorides, e.g. 4-chlorobuta-1,2-diene[25], 1-chloro-3-methylbuta-1,2-diene[26], and 1-chloro-3-ethylpenta-1,2-diene[27], for instance:

$$CHCl=C=CR-CH_2-R \longrightarrow HC\equiv C-CR=CH-R.$$

The removal of hydrogen halides from the acetylenic halogen derivatives of the type $R-C\equiv C-CR_2^1Cl$ or $R'C\equiv C-CH_2-CHCl-R$ is only recommended for cases where R = aryl[28,29]. In other cases the yield of vinylacetylenes is usually small[30-34].

Metal acetylides can sometimes be used as acceptors for hydrogen halides[34-38]. For instance, the reaction of sodium acetylide with 1,3-dibromopropane besides hepta-1,6-diyne also yields, judging from the physical constants, vinylmethylacetylene[38]. However, the workers who studied this reaction wrongly assumed that they had obtained propenylacetylene.

The reaction of alcoholic alkali with 1,2,3,4-tetrabromoalkanes yields vinylacetylenes instead of the expected diacetylenes: a reduction takes place at the same time[39,40,41]. A convenient method for the preparation of vinylacetylene is the treatment of 1,2-dichlorobut-2-ene or the Δ^3-analogue with the solution of sodium amide in liquid ammonia[42]. Vinylacetylene can also be obtained in good yields by dehydrochlorinating 1,3-dichlorobut-2-ene (a by-product in the manufacture of chloroprene) with KOH in glycol[43]. Dehydrohalogenation also yields vinylacetylenic halogen derivatives[44,45] and ethers[46].

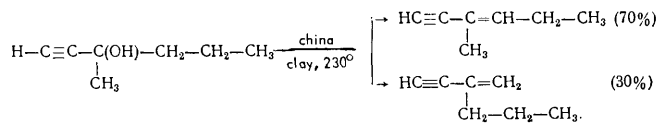
Vinylacetylene is formed in the reduction of some polyhalides by zinc[47,48].

2. Dehydration of Acetylenic Alcohols

This is a most convenient and frequently used general method for the preparation of enyne hydrocarbons, especially the branched ones. α-Acetylenic acid and alkylpropargyl alcohols are in their turn easily prepared from carbonyl compounds by Grignard reagents[49], Favorskii's reaction[14], or the reaction with acetylene and sodium amide in liquid ammonia[50]. β-Acetylenic alcohols can be prepared from propargyl bromide and aldehydes by Reformatski's reaction[51,52] or by the reaction of epoxides with acetylides in liquid ammonia[53].

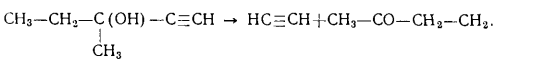
Dehydration of tertiary dialkylpropargyl alcohols is usually carried out by passing them over $MgSO_4$ [54,55] or $AlPO_4$ [56-58] at 230°–250°, or by heating them with 30% H_2SO_4 [59,60], acetic anhydride and H_2SO_4 [61], H_3PO_4 [62,63], or HCl [64]. There is a number of other dehydration catalysts: aluminium oxide[65-67], acid and basic sulphates[68-70], toluenesulphonic acid[71-73], china clay[74], $CuSO_4$ [75,76], oxalic acid[75,76], etc.[78-81]. The formation of enyne hydrocarbons has been repeatedly observed during the preparation of chlorides from dialkylpropargyl alcohols by the action of HCl [82-84]. In the dehydration of asymmetrically substituted dialkylpropargyl alcohols the hydrogen atom is split off mainly

from the larger radical, for instance [10,57,61,62,74,85,86]:

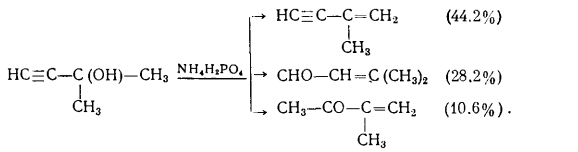


It was not possible to obtain 2-trifluoromethylbut-1-en-3-yne by the dehydration of the corresponding tertiary alcohol [87].

The dehydration of tertiary acetylenic alcohols with cyclic substituents can be carried out with $POCl_3$ in pyridine [88-92]. Tertiary acetylenic alcohols containing phenyl radicals are often dehydrated during distillation [93] or in the presence of acid reagents [94-95]. Dehydration in the presence of heterogeneous catalysts is often accompanied by the formation of considerable quantities of by-products [65,96,97]. Thus, over aluminium oxide, at 230°, alcohols are decomposed into acetylene and ketone to a considerable extent [65]:

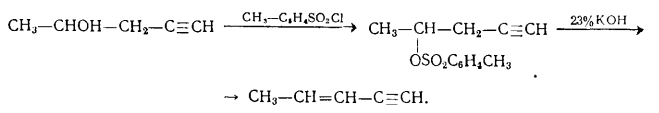


Over phosphates alcohols are isomerised to aldehydes and ketones [96,97]:

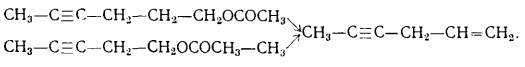


Acetylenic alcohols which do not contain the terminal ethynyl group yield better results [65,66]. Isomerisation of tertiary alcohols occurs under the action of formic acid or P_2O_5 in benzene [98]. Good yields of vinylacetylenic hydrocarbons are only obtained with aromatic alcohols [99].

Dehydration of secondary alkylpropargyl alcohols is more difficult: at 325° and over aluminium oxide hydrocarbons are only obtained from alcohols which do not contain the terminal ethynyl group [67]. For the preparation of hydrocarbons from β-acetylenic alcohols a method based on the preliminary formation of sulphonic esters can be used [100-104]:



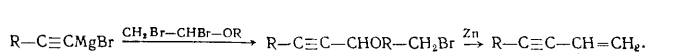
Primary α- and secondary β-acetylenic alcohols can be converted to hydrocarbons by the pyrolysis of their respective acetates [105-107]:



Vinylacetylenic hydrocarbons can also be prepared by the pyrolysis of dialkylpropargyl phenyl ethers [108], and, possibly, of acetals containing a vinylethynyl group [109].

3. Splitting of the Elements of Alkylhypohalogenites from Acetylenic β-Halogeno-Ethers

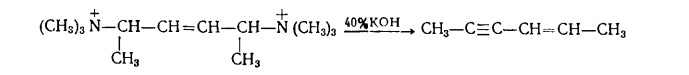
Acetylenic β-halogeno-ethers are easily prepared by the action of metal acetylides on α, β-dibromo-ethers. The elements of alkylhypohalogenites are removed by heating with zinc, giving good yields of vinylacetylenic hydrocarbons [110,114]:



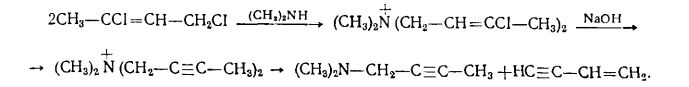
Vinylacetylene [110] and a series of its homologues and phenyl-substituted derivatives were prepared in this way, as well as some hydrocarbons containing isolated multiple bonds [114].

4. Exhaustive Methylation of Unsaturated Amines

Vinylacetylene [9,115,116] and vinylmethylacetylene [4-8,117,118] were first prepared by the decomposition of the products from the exhaustive methylation of unsaturated amines. The method was subsequently used repeatedly for the preparation of these hydrocarbons, and more recently for the preparation of hex-2-en-4-yne [119]:



A study was made of the synthesis of vinylacetylene by amination and subsequent exhaustive methylation of 1,3-dichloro but-2-ene, a by-product in the manufacture of chloroprene. Vinylacetylene was recovered in yields above 70% [115,116]:



5. Selective Hydrogenation of Diacetylenes

This reaction usually yields dienes [120]. In some cases, however, it is possible to stop the hydrogenation at the enyne stage. For instance, the reduction of hydrocarbons containing one of the triple bonds in the terminal position by sodium in liquid ammonia yields the corresponding enyne hydrocarbons as the terminal triple bond resists hydrogenation [121]. This method has no preparative importance as diacetylenes are not easily accessible.

B. PREPARATION FROM COMPOUNDS WITH A SMALLER NUMBER OF CARBON ATOMS

1. Dimerisation of Acetylenic Hydrocarbons

Soon after its discovery [1], the polymerisation of acetylene to mono- and divinylacetylenes in the presence of copper complexes was reproduced by Klebanskii [122-143] and Zelinskii [124]; Nieuwland et al. had not given a detailed account regarding the procedure. Many papers and patents [122-143] are devoted to the mechanism and the conditions of this reaction, which is the basis of the production of chloroprene from acetylene. The main difficulty lies in arresting the polymerisation at the dimer stage, i.e. monovinylacetylene, and various improvements of the original method concern this particular

step. If no special measures are taken, the reaction products are two trimers (divinylacetylene and ethynylbutadiene) and higher polymers.

In Klebanskii's opinion an ionic mechanism underlies acetylene polymerisation, the principal part being played by the acidic properties of acetylene complexes with cuprous chloride[122,125,126]. Different variations of the ionic mechanism were also suggested by other investigators[132,134]. Hypotheses involving the intermediate formation of copper acetylides or of copper acetylide complexes were also advanced[125,131].

This reaction cannot be used effectively for the synthesis of vinylacetylene homologues, although by this method acetylene and methylacetylene yielded small amounts of vinylmethylacetylene[144]:

$$CH_3{-}C{\equiv}CH + HC{\equiv}CH \longrightarrow CH_3{-}C{\equiv}C{-}CH{=}CH_2.$$

A series of workers showed vinylacetylene to be the primary product in acetylene polymerisation under different conditions[128], including the photochemical reaction[145,146] and the high-temperature and electrical cracking[143,147-151]. Vinylacetylene can be isolated from acetylene mixtures obtained by pyrolysis. A number of papers and patents[152-162] are devoted to the isolation of vinylacetylene from various gas mixtures, as well as to the analysis and purification of such mixtures.

2. Reactions of Metal Acetylides with Halogen Derivatives

These were used chiefly for the synthesis of enyne hydrocarbons with isolated multiple bonds. In the reaction of acetylenic Grignard reagents, or sodium acetylides with allyl bromide or allyl benzenesulphonate, good yields of allylacetylene and a series of its homologues were obtained[163-166]:

$$R{-}C{\equiv}C{-}MgBr + Br{-}CH_2{-}CH{=}CH_2 \xrightarrow{CuCl} R{-}C{\equiv}C{-}CH_2{-}CH{=}CH_2.$$

The reaction of allyl bromide with sodium acetylide gave a small yield of vinylmethylacetylene (I) involving a multiple bond migration[167]. The main reaction product was a hydrocarbon of structure (II):

$$HC{\equiv}CNa + Br{-}CH_2{-}CH{=}CH_2 \begin{cases} \rightarrow CH_3{-}C{\equiv}C{-}CH{=}CH_2 & (I) \\ \rightarrow HC{\equiv}C{-}\underset{\displaystyle CH{=}CH_2}{\underset{|}{CH}}{-}CH_2{-}CH{=}CH_2 & (II). \end{cases}$$

This method can be used for preparing aliphatic, alicyclic, and aromatic enyne hydrocarbons with one or several carbon atoms separating the multiple bonds[168-172]. There are patents on this subject, but they require testing[173].

Propargyl organometallic compounds can also react with active halogen derivatives, to yield enyne hydrocarbons[174].

3. Reactions of Propargyl Halides with Unsaturated Organometallic Compounds

These reactions, for instance with vinyl- and allyl-magnesium bromide also give enyne hydrocarbons, but in some cases they are obtained with an admixture of the isomeric vinylallenes[169,175,176]:

$$HC{\equiv}C{-}CH_2Br + BrMg{-}CH{=}CH_2 \begin{cases} \longrightarrow HC{\equiv}C{-}CH_2{-}CH{=}CH_2 \\ \longrightarrow CH_2{=}C{=}CH{-}CH{=}CH_2. \end{cases}$$

4. Alkylation of Vinylacetylene

Alkylation of vinylacetylene and its homologues containing a terminal ethynyl group is a convenient method for preparing vinylalkylacetylenes. The reaction is usually carried out in liquid ammonia with sodium amide. Alkyl halides and dialkyl sulphates are used as alkylating agents. This method was used for preparing vinylalkynes with alkyl radicals ranging from methyl to octyl inclusive, in yields of 80%. With the lower alkyl groups, the yield was diminished owing to the evaporation of the hydrocarbon together with the ammonia[177-179]. In some cases of alkylation in the presence of excess sodium amide the migration of multiple bonds towards the end of the molecule was observed[180]. This reaction does not work with secondary or tertiary alkyl halides.

$$R{-}Br + NaC{\equiv}C{-}CH{=}CH_2 \longrightarrow R{-}C{\equiv}C{-}CH{=}CH_2.$$

Good results are also obtained in alkylations of vinylacetylene Grignard reagents[181].

5. The Wittig Reaction

The Wittig reaction can be used for preparing enyne hydrocarbons from saturated halogen derivatives and acetylenic aldehydes according to the scheme[182].

$$R{-}CH_2Br \xrightarrow{(C_6H_5)_3P} [R{-}CH_2\overset{+}{P}(C_6H_5)_3]\,\overset{-}{Br} \xrightarrow{C_6H_5Li} R{-}CH{=}P(C_6H_5)_3 \rightarrow$$
$$\xrightarrow{HC{\equiv}C{-}CHO} R{-}CH{=}CH{-}C{\equiv}CH.$$

C. PREPARATION OF ENYNE HYDROCARBONS FROM COMPOUNDS WITH A LARGER NUMBER OF CARBON ATOMS. DECOMPOSITION OF ACETYLENIC GLYCOLS

Decomposition of vinylacetylenic tertiary alcohols with alkali[183,184] yields vinylacetylenes:

$$R_2C(OH){-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{KOH} R_2CO + HC{\equiv}C{-}CH{=}CH_2.$$

Vinylacetylenes are also obtained by the decomposition in the presence of sulphuric acid of some acetylenic glycols containing phenyl groups[185,186]:

$$C_6H_5{-}C{\equiv}C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}(OH){-}\underset{\displaystyle CH_3}{\underset{|}{C}}(OH){-}C_6H_5 \rightarrow C_6H_5{-}C{\equiv}C{-}CH{=}CH_2 + CH_3{-}CO{-}C_6H_5.$$

II. PHYSICAL PROPERTIES OF ENYNE HYDROCARBONS

Only the first member in the series of vinylacetylenic hydrocarbons is gaseous at room temperature. The other hydrocarbons are liquid or solid. The physical properties

of vinylacetylene have been studied in greater detail than those of other enyne hydrocarbons. Its principal constants are given in Table 1.

TABLE 1. The principal physical constants of vinylacetylene.

Boiling point (760 mm) [187]	5.11°C	refractive index n_D (1^0) [190]	1.4161
Vapour pressure [1,188]		thermal conductivity ($\lambda \times 10^4$ at 70°) [191]	0.437
at -10°C	401.0 mm	heat capacity (C_p^0) [191,192]	
at 0°C	621.0 mm	at 298.16°K	17.49 cal × × deg^{-1} mole^{-1}
at +12°C	952.0 mm	at 1500°K	37.52 cal × × deg^{-1} mole^{-1}
Density [1,189]		viscosity ($\eta \times 10^4$)	
at -10°C	0.7187	at 40°C [191]	0.865
at 0°C	0.7095	solubility in water	
at +30°C	0.6679	at 0°C [193]	1.04%

Intermediate vapour pressures of vinylacetylene can be calculated from the formula

$$\log P_{(mm)} = 6.08797 - \frac{620.161}{187.960\ t^0}\ ^{194},$$

and those of the specific gravity in the temperature range from -3° to -80°, from the formula

$$d_4^t = 0.7095 - 0.00114\,t^0\ ^{142}.$$

The effect of an electric field [195] on the thermal conductivity of gaseous vinylacetylene was also studied. Heats of evaporation were not determined experimentally, but they were calculated for the temperature range -80° to +168° [195,197] and tabulated.

Data are available on certain other thermodynamic functions [192,198-202]. The energy of the first electron in excited state was calculated [203]. Explosive properties of vinylacetylene have been investigated [204,205]: concentrations in

TABLE 2. Principal constants of enyne hydrocarbons.

Hydrocarbon	B.p., °C	d_4^{20}	n_D^{20}	Method of prep.	Reference
$HC\equiv C-CH=CH-CH_3$	46—48	—	1.4356(19)	A2	33
cis	44.5—44,6	—	1.4377(16.5)	A2	100
trans	52—52.2	—	1.4407(16.5)	A2	100
	51.9	0.7270	1.4377	A2	101
$HC\equiv C-CH=CH-C_6H_5$	72—74	0.7425	1.4381	A2	51
$HC\equiv C-CH=C(CH_3)_2$	81—83	0.7537	1.4504	B4	180
	73—75	—	—	A2	70
$HC\equiv C-CH=CH-CH(CH_3)_2$	117—120	—	—	A1	11
$HC\equiv C-CH=CH-C_4H_9$	126—129	—	1.4431(22)	A2	103
$HC\equiv C-CH=CH-CH_2CH(CH_3)_2$	126—129	—	—	A1	12
$HC\equiv C-CH=CH-C(CH_3)_3$	?—	—	—	—	207
$HC\equiv C-CH=CH-C_4H_{13}$	57—58(11)	0.7822	1.4508	A2	104
$HC\equiv C-CH=CH-C_8H_{17}$	65(10)	—	1.4500(22)	A2	103
$HC\equiv C-CH=CH-C_{11}H_{23}$					
cis	m.p. 41—42°	—	—	B5	182
trans	m.p. 46.5—47.5°	—	—	B5	182
$HC\equiv C-C(CH_3)=CH_2$	32—32.5	0.7044	1.4151	A2	207
	32—32.5	—	1.4158	A2	10
$HC\equiv C-C(CH_3)=CH-CH_3$	67—69	—	1.4332	A2	10
	66—67	0.739	1.4310	A2	75
$HC\equiv C-C(CH_3)=CH-CH_2-CH_3$	91—94	—	1.4304(22)	A2	86
	93	—	—	A2	85
$HC\equiv C-C(CH_3)=CH-C_6H_7$	44—45(50)	0.776	1.4395	A2	74
$HC\equiv C-C(CH_3)=CH-CH(CH_3)_2$	104.5	—	—	A2	61
$HC\equiv C-C(CH_3)=CH-C_4H_{11}$	53(11)	—	1.4464(22)	A2	57
$HC\equiv C-C(C_2H_5)=CH-CH_3$	96.5	0.7886(25)	1.4338(25)	A2	72
	41—43(100)	0.7733(13)	1.4396(a,13)	A2	26
$HC\equiv C-C(C_3H_7)=CH-C_2H_5$	136—137	0.7799(25)	1.4432(25)	A2	72
$HC\equiv C-C(CH(CH_3)_2)=CH_2$	41(30)	0.7916	1.4532	A2	74
$HC\equiv C-C(C(CH_3)_3)=CH_2$	97.5—98	0.7544	1.4330	A2	207
	98	0.7643(16.5)	1.4280(a,16.5)	A2	54
$HC\equiv C-C(C(CH_3)_3)=CH-CH_3$	123—124	—	1.4470	A2	98
$HC\equiv C-C(C(CH_3)_3)=CH_2$	128	—	1.4410	A2	9
$HC\equiv C-C(C(CH_3)_2-C_2H_5)=CH-CH_3$	148	—	1.4500	A2	98
$CH_3-C\equiv C-CH=CH_2$	59—59.5	0.7402	1.4490	B4	208
	59.4	0.7339(25)	1.4467(25)	A4	6
$C_2H_5-C\equiv C-CH=CH_2$	83.5—84	0.7486	1.4519	B4	208
	83(747)	0.7480	1.4523	B4	181
$C_3H_7-C\equiv C-CH=CH_2$	108.5—109	0.7626	1.4626	B4	208
	44.3—44,7 (77)	0.7579(25)	1.4520(25)	A3	111
$C_4H_9-C\equiv C-CH=CH_2$	62—62.5(60)	0.7713	1.4560	B4	208
	61.5—62(60)	0.7671(25)	1.4505(25)	A3	111
$(CH_3)_2CH-CH_2-C\equiv C-CH=CH_2$	54—56(60)	0.7668	1.4440	B4	178
$C_6H_{11}-C\equiv C-CH=CH_2$	59.5—60(20)	0.7782	1.4580	B4	179
	27.7—28.2 (4)	0.7602(25)	1.4487(25)	A3	111
$(CH_3)_2CH-(CH_2)_2-C\equiv C-CH=CH_2$	76—77(60)	0.7803	1.4571	B4	178
$C_4H_{13}-C\equiv C-CH=CH_2$	76—76.5(20)	0.7873	1.4598	B4	179
	45—45.5(4)	0.7872(25)	1.4565(25)	A3	111
$C_7H_{15}-C\equiv C-CH=CH_2$	74.5(9)	0.7962	1.4606	B4	177
$C_8H_{17}-C\equiv C-CH=CH_2$	110.5—111 (20)	0.7964	1.4620	B4	179
	77.5—78(4)	0.7858(25)	1.4510(25)	A3	111
$CH_3-C\equiv C-CH=CH-CH_3$	88—89	0.7710	1.4918	A4	119
	91—92	0.7703	1.4634	A2	67
$C_4H_9-C\equiv C-CH=CH-CH_3$	70—70.5(29)	0.7832(25)	1.4590(25)	A3	111
$C_5H_{11}-C\equiv C-CH=CH-CH_3$	54.5—55(5)	0.7850(25)	1.4609(25)	A3	111
$C_6H_{13}-C\equiv C-CH=CH-CH_3$	45—45.4(4)	0.7872(25)	1.4565(25)	A3	111
$CH_3-C\equiv C-CH=C(CH_3)_2$	56—57(90)	0.7849	1.4659	A2	67
$CH_3-C\equiv C-C(CH_3)=CH_2$	82—83	0.7518	1.4512	B4	179
	75—77	—	1.4002	A2	108
$C_2H_5-C\equiv C-C(CH_3)=CH_2$	104.5—105.5	0.7572	1.4518	B4	179
$C_3H_7-CH(CH_3)-C\equiv C-CH=CH_2$ / $CH_3-CH=C(C_3H_7)-C\equiv C-CH_3$	139—140	0.7622	1.4450	A1	37
$(CH_3)_2C-C\equiv C-C(CH_3)=CH_2$?	58(100)	0.7622	1.4385	A1	35
$CH_3-C\equiv C-C(CH_3)=CH_2$	59—60(50)	0.7808	1.4518	B4	179
$C_2H_5-C\equiv C-C(CH_3)=CH_2$	74—74.5 (50)	0.7774	1.4518	B4	179
$CH_3-C\equiv C-C(CH_3)=CH-CH_3$	107—108	0.7883	1.4480	A2	84
$(CH_3)_2CH-C\equiv C-C(CH_3)=CH-CH_3$	67—70(30)	—	1.3949(22)	A2	66
$CH_3-C\equiv C-C(CH_3)=CH-C_6H_5$	80—85(30)	—	1.4158(22)	A2	66
$C_4H_9-C\equiv C-C(CH_3)=CH-CH_3$	80—82(30)	—	1.4638(22)	A2	65
$(CH_3)_2C-C\equiv C-C(CH_3)=CH-CH_3$	75—80(30)	—	1.3881(22)	A2	66
$C_4H_9-C\equiv C-C(CH_3)=CH-C_6H_5$	94—97(30)	—	1.4662(22)	A2	72
$C_4H_9-C\equiv C-C(CH_3)=CH-C_4H_9$	149—152(30)	—	1.4662(22)	A2	72
$C_4H_9-C\equiv C-C(CH_3)=C(CH_3)_2$	115—117(15)	—	1.4668(22)	A2	66
$(CH_3)_2C-C\equiv C-C(CH_3)=C(CH_3)_2$	58.5(7)	0.7778	1.4518	A1	36
$HC\equiv C-CH_2-CH=CH_2$	41.5—42.5	0.7246	1.4152(19)	A3	114
	42—43	0.7320(19)	1.4184(19)	B3	175

TABLE 2 (contd.)

Hydrocarbon	B.p., °C	d_4^{20}	n_D^{20}	Method of prep.	Reference
$HC\equiv C-CH_2-CH=CH-CH_3$	75—76	0.7558	1.4290	A3	114
$HC\equiv C-CH_2-CH=CH-C_2H_5$	102	0.7635	1.4375	A3	114
$HC\equiv C-CH_2-CH=C(CH_3)_2$	101	0.771	1.4464	A2	63
$HC\equiv C-CH_2-C(CH_3)=C(CH_3)_2$	112—113	0.788	1.4293	A2	63
$HC\equiv C-CH_2-C(CH_3)_2-CH=CH_2$	126	0.799	1.4348	A2	63
$CH_3-C\equiv C-CH_2-CH=CH_2$	86—86.5	0.7630	1.4368	B2	166
	87(753)	0.767(14)	1.446(14)	A2	107
$C_4H_9-C\equiv C-CH_2-CH=CH_2$	58(22)	0.7770(25)	1.4413(25)	B2	165
$C_7H_{11}-C\equiv C-CH_2-CH=CH_2$	73—74(22)	0.7850(25)	1.4444(25)	B2	165
	73—74(22)	0.7880	1.4450	B2	163
$HC\equiv C-(CH_2)_2-CH=CH_2$	70	0.8579 (18.2)	—	A1	2
$HC\equiv C-(CH_2)_2-CH=CH-C_6H_7$ (*trans*)	144—145	—	1.4520—1.4525	B2	174
$C_5H_{11}-C\equiv C-(CH_2)_2-CH=CHC_5H_{11}$	?	—	—	—	209
$HC\equiv C-(CH_2)_3-CH=C(CH_3)_2$	128—129	0.7816(19)	1.4418(16)	B2	172
$HC\equiv C-(CH_2)_4-CH=CH_2$	122	—	1.4310—1.4325	B2	171
$HC\equiv C-(CH_2)_4-CH=CH-C_3H_7$	77—78(19)	—	1.4480(18)	A5	121
cis	73(10)	—	1.4462	B2	169
trans	82—84(18)	—	1.4462	B2	170
$HC\equiv C-C(=CH-(CH_2)_2)$	57—59(100)	0.8596	1.4891	A2	92
$HC\equiv C-C(=CH-(CH_2)_4)$	53—56(40)	—	1.4978	A2	88
	47—49(20)	0.9032	1.4956	A2	92
$HC\equiv C-C(=CH-(CH_2)_3)$	78(35)	—	1.4790(19)	A2	58
$HC\equiv C-C(=CH-CH_2-CH(CH_3)-(CH_2)_2)$	160	0.8560	1.4648	A1	21
$HC\equiv C-C(C(CH_3)-(CH_2)_3-C(CH_3)_2)$	68—69(18)	—	1.4925(14)	A2	90
$CH_3-C\equiv C-C(=CH-(CH_2)_4)$	165—167	0.8600	1.4469	B4	21
$CH_3-C\equiv C-C(=CH-CH_2-CH(CH_3)-(CH_2)_2)$	175	0.859	1.4654	B4	21
$C_4H_9-C\equiv C-C(=CH-(CH_2)_4)$	68(0.6)	—	1.5000	A2	88
$C_4H_9-C\equiv C-C(=C(CH_3)-(CH_2)_3-C(CH_3)_2)$	133—134(12	—	1.4800	A2	90

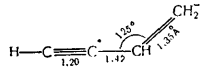
Hydrocarbon	B.p., °C	d_4^{20}	n_D^{20}	Method of prep.	Reference
$HC\equiv C-CH(-CH=CH-(CH_2)_3)$	97.2(752)	0.8014	1.4363	B2	168
$HC\equiv C-CH_2-C(=CH-(CH_2)_4)$	56(12)	—	1.4835(21,5)	—	70
$C_6H_{11}-C\equiv C-CH-CH=CH-(CH_2)_3$	120(15)	0.976	1.4809	B2	21
$C_6H_{11}-CH_2-C\equiv C-CH-CH=CH-(CH_2)_3$	150(15)	0.962	1.5048	B2	21
$C\equiv C-(CH_2)_3-CH=CH-(CH_2)_4$	100(20)	—	1.5078(25)	—	210
$HC\equiv C-CH=CH-C_6H_5$	59(2)	0.9640	1.6123	A1	29,52
	65—67(4)	0.9784	1.6047	A1	92
$C_6H_5-C\equiv C-CH=CH_2$	85—86(15)	0.9480	1.6018	A3	113
	96(20)	0.9480	1.6018	A1	28
$C_6H_5-C\equiv C-CH=CH-CH_3$	66—67(1)	0.9448	1.5893	A2	99
$C_6H_5-C\equiv C-CH=CH-C_2H_5$	71—72(1)	0.932	1.5802	A2	99
$C_6H_5-C\equiv C-CH=CH-C_3H_{11}$	110—111(1)	0.9167	1.5508	A2	77
$C_6H_5-C\equiv C-CH=CH-C_6H_5$	144—146(2)	—	1.5613	A2	19
$C_6H_5-CH_2-C\equiv C-CH=CH-CH_3$	40(04)	0.9450(26.5)	1.5510(26.5)	A2	19
$C_6H_5-C\equiv C-C(=CH_2)(CH_3)$	87—89(7)	0.9425	1.5750 (α)	A2	94
$C_6H_5-C\equiv C-C(=CH_2)(C(CH_3)_2)$	115—116(10)	—	—	A2	14
$C_6H_5-C\equiv C-C(=CH-CH_3)(CH_3)$	113—115(9)	0.9305	1.5828(13)	A2	15,16
$C_6H_5-C\equiv C-C(=C(CH_3)_2)(CH_3)$	120—122(12)	0.9254	—	A2	14
$C_6H_5-C\equiv C-C(=CH-C_4H_{11})(CH_3)$	141—142(5)	—	—	A2	178
$C_6H_5-C\equiv C-CH_2-CH=CH_2$	103—105(20)	0.940(15)	1.5580(18)	B2	164
	107—108(22)	0.932	1.5574	B2	165
$HC\equiv C-CH(C_6H_5)-CH=CH_2$	60.5—61 (1.6)	0.9214(25)	1.5228(25)	B3	176
$C_6H_5-C\equiv C-C(=CH-(CH_2)_4)$	167—170 (16)	—	—	A2	180
$C_6H_5-C\equiv C-CH-CH=CH-(CH_2)_3$	160(15)	0.997	1.5516	B2	21
$(C_6H_5)_2C-C\equiv C-CH=CH_2$	134—135 m.p.			B4	450

Note: 1) The pressure at the boiling points is given in brackets. 2) The temperature at which the refractive indices and specific gravities were measured is given in brackets. Temperature is not indicated for the data obtained at 20°. 3) Hydrocarbons prepared by dehydration of unsymmetrical dialkylpropargyl alcohols (A2) consists of a mixture of two isomers. The formula given in the table is that of the predominant isomer. 4) The best available data on phenyl-substituted enynes have been selected.

explosive mixtures with air range from 2.13–22.92% [204]. The solubility of vinylacetylene in water decreases with rise in temperature and on saturation of the solution with sodium chloride [193].

The principal constants of vinylacetylene homologues and of other enyne hydrocarbons are given in Table 2 which shows that the boiling points of enyne hydrocarbons are closely dependent on their structure. For instance, of all the isomers with five carbon atoms, vinylmethylacetylene has the highest, and isopropenylacetylene the lowest boiling point. Hydrocarbons with conjugated multiple bonds have a higher boiling point than their isomers with the same skeletal structure but with isolated bonds. Vinylalkynes have the highest refractive index of all the hydrocarbons with conjugated multiple bonds and a straight chain. Attempts have been made to calculate densities and refractive indices of vinylacetylenes, as well as those of other hydrocarbons [211].

Electron-diffraction data. Electron-diffraction patterns for vinylacetylene and vinylmethylacetylene show their spatial configuration to be as follows [7,212]:



Few thermodynamic data are available for vinylacetylene homologues. They include heats of formation, heats of dissociation, and enthalpies for gaseous allyl-, isopropenyl-, and vinylmethylacetylenes [213], as well as the thermal conductivity of gaseous isopropenylacetylene [214] and its rate of combustion [215].

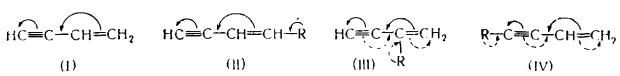
Molecular refractions found experimentally for enyne hydrocarbons with isolated multiple bonds are close to the calculated values. In the case of vinylacetylene, however, there is a considerable exaltation [216]. The highest exaltation is observed in the vinylalkyne series (1.1–1.4). The value falls when groups are attached to the β-carbon atom of the double bond. The exaltation of the molecular refraction of vinylacetylenes is somewhat lower than that of 1, 3-dienes.

TABLE 3. Dipole moments of vinylacetylene and its homologues.

Hydrocarbon	μ, Debye	Hydrocarbon	μ, Debye
$HC\equiv C-CH=CH_2$	0.77	$C_3H_7-C\equiv C-CH=CH_2$	0.65
$HC\equiv C-CH=CH-CH_3$, *cis*	0.85	$C_4H_9-C\equiv C-CH=CH_2$	0.63
trans	0.93	$C_5H_{11}-C\equiv C-CH=CH_2$	0.65
$HC\equiv C-\underset{\underset{CH_3}{|}}{C}=CH_2$	0.55	$C_6H_{13}-C\equiv C-CH=CH_2$	0.67
		$C_8H_{17}-C\equiv C-CH=CH_2$	0.68
$HC\equiv C-\underset{\underset{C(CH_3)_3}{|}}{C}=CH_2$	0.69	$C_6H_5-C\equiv C-CH=CH_2$	0.27
		$CH_3-C\equiv C-\underset{\underset{CH_3}{|}}{C}=CH_2$	0.65
$HC\equiv C-CH=CH-C_6H_5$	0.97		
$CH_3-C\equiv C-CH=CH_2$	0.57	$CH_3-C\equiv C-\underset{\underset{C(CH_3)_3}{|}}{C}=CH_2$	0.67
$C_2H_5-C\equiv C-CH=CH_2$	0.62		
		$C_2H_5-C\equiv C-\underset{\underset{C(CH_3)_3}{|}}{C}=CH_2$	0.64

Dipole moments (Table 3) were measured for a series of enyne hydrocarbons of different structures containing conjugated multiple bonds[179,208,217]. Owing to conjugation, the dipole moment of vinylacetylene is somewhat lower than that of ethylacetylene (0.80 Debye). Substitution of the acetylenic hydrogen or the hydrogen attached to the β-carbon atom of the ethylenic bond by an alkyl or, especially, a phenyl radical results in a sharp drop in the dipole moment. On the other hand, the substitution of a terminal hydrogen of the vinyl group causes a sharp increase in the dipole moment. Dialkyl derivatives, with the substituents at the acetylenic and "inner" carbon atoms of the double bonds have dipole moments approximately the same as vinylalkynes.

Dipole-moment values support the hypothesis of the shift of electron density in vinylacetylenic hydrocarbons under the influence of substituents. The electron-density shift is represented by arrows in formulae (I)–(IV):



(I) (II) (III) (IV)

Ultra-violet spectra. Enyne hydrocarbons with isolated multiple bonds absorb only in the vacuum region [< 300 mμ (Ed. of Translation)]. Vinylacetylene, its homologues and derivatives give absorption maxima in the region at the limit of the sensitivity of ordinary spectrophotometers (~ 220 mμ) with a characteristic inflection at ~ 228 mμ. Diene hydrocarbons absorb in approximately the same region, but with higher intensity and without the inflection[81,100,218-224]. Aromatic vinylacetylenes give absorption maxima at ~ 250 mμ[81].

Infra-red spectra. Infra-red spectra of numerous vinylacetylenic hydrocarbons of different structure are available in the literature[100,121,179,192,223,225-232], but the theoretical frequencies have only been worked out for vinylacetylene[192,226,233].

Spectra of enyne hydrocarbons with isolated bonds consist of the ordinary absorption bands, characteristic of olefines and acetylenes of analogous structure[230]. In the spectra of vinylacetylene and its homologues the frequencies of the stretching vibrations of the triple, and especially the double bond, are considerably lower than in unconjugated systems. The stretching frequency of the double bond in the spectra of alkenylacetylenes is somewhat higher (1620 cm^{-1}) than in those of vinylalkynes (1608 cm^{-1})[230].

Frequencies characteristic of a terminal ethynyl group are 2114 and 3300 cm^{-1}, whereas disubstituted acetylenes absorb at 2230–2235 cm^{-1}. The intensity of the double-bond band is considerably higher for vinylalkynes and isoalkenylacetylenes, containing an unsubstituted methylene group, than for alkneylacetylenes. This property of the spectra may be related to the reactivity of the double bond with respect to electrophilic reagents[230].

The spectra of enynes exhibit a general pattern related to the structure of the hydrocarbons. For instance, characteristic high intensity bending frequencies near 910 and 972 cm^{-1} correspond to the vinyl group, a frequency near 955 cm^{-1}, to the $-CH=CH-$ group (of especially high intensity for the *trans*-isomer)[100], and a frequency at 890–900 cm^{-1}, to the isopropenyl group. Vinylalkynes have a high-intensity frequency for the stretching CH-vibrations at ~3100 cm^{-1}. Most vinylacetylenes absorb at 1660–1790 cm^{-1}, a frequency characteristic of acetylenes, but of unexplained origin. The presence of a t-butyl radical gives rise to absorption in the region 1200–1250 cm^{-1}[179,230].

In the spectra of phenyl-substituted vinylacetylenes the enyne system is characterised by frequencies of 1600, 2094, and 2103 cm^{-1} for monosubstituted, and 1631, 2184, 2200–2220, and 2245 cm^{-1} for disubstituted acetylenes. Thus, the vibration frequencies corresponding to the double bond are lower than those for olefines when the bond is located between the phenyl and acetylenic groups[18,231].

Infra-red spectra can be used for the determination of vinylacetylene impurities in industrial products[232].

Raman spectra have been studied to a lesser degree than infra-red[35,36,52,233-237]. In the Raman spectra of vinylalkynes the double bond is represented by the high-intensity frequency of ~ 1606 cm^{-1} and in those of alkenylacetylenes by the frequency of ~ 1616 cm^{-1}. The terminal ethynyl group is characterised by a high-intensity frequency of ~ 2100 cm^{-1}, and a low intensity one of ~ 3300 cm^{-1}, and the disubstituted acetylenic group, by frequencies of 2230 (very high intensity) and 2330 cm^{-1} (medium intensity)[215]. In the spectra of allylacetylene and allylmethylacetylene the triple bond gives rise to a high-frequency band of 2124 cm^{-1} (there is no conjugation)[216,236]. Bending CH vibrations of ethylenic groups are represented by a medium-intensity frequency of 920 cm^{-1}, or a low-intensity one of 950 cm^{-1} (depending on the structure).

The conjugated system in aromatic vinylacetylenes is characterised by frequencies as follows:
$C_6H_5-CH=CH-C\equiv CH$ 1611, 2104 cm^{-1}; and
$C_6H_5-C\equiv C-CH=CH_2$ 1630, 2186, and 2223 cm^{-1}[18,237].

Microwave spectra have been studied only for vinylacetylene[238].

Mass-spectra have been measured for vinylacetylene and 6 homologues of different structure[239-242]. The highest intensity in the mass-spectra of vinylacetylene and its three nearest homologues are due to molecular ions. Ionised residues are formed primarily by the rupture of the

C–H bond. The curve, obtained for the homologues by plotting the ion distribution against the number of carbon atoms contains two maxima (for $C_3H_x^+$ and $C_5H_x^+$ ions). The first one is characteristic of all hydrocarbons. Of all ions formed by the breaking of the C–C– bond, the one with a mass of 39 has the highest energy. Further loss of hydrogen by the initially formed ionised residues is characteristic of all isomers.

Determinations of ionisation potentials showed isopropenylacetylene to be the most difficult to ionise (ionisation potential 10.1 eV). Vinylmethylacetylene (9.4 eV) and especially propenylacetylene (8.5 eV) have considerably lower ionisation potentials than vinylacetylene (9.9 eV).

Increase in the chain length of the radical attached to the triple bond results in reduced stability of the molecular ion and an increase in the energy of ionised residues formed by the breaking of C–C– bonds. $C_3H_x^+$ and $C_6H_x^+$ ions have the maximum energy. The ions predominating among the ionised residues — $C_nH_{2n-3}^+$, $C_nH_{2n-5}^+$, $C_nH_{2n-7}^+$, as well as $C_nH_{2n-4}^+$ — are probably stabilised by conjugation. The ionisation potential drops with increase in chain length.

Polarographic curves have been obtained for 12 vinylacetylenic hydrocarbons of different structure[243,244]. Only conjugated enynes are reduced at the dropping mercury electrode. Allylmethylacetylene, containing isolated multiple bonds, is not reduced[244].

Vinylacetylene ($E_{\frac{1}{2}}$ = 2.4 eV) is reduced rather more easily than butadiene, and with greater difficulty than diacetylene. The nearest homologues are more difficult to reduce than the unsubstituted compound ($E_{\frac{1}{2}}$ = 2.5–2.6 eV). The position of one methyl group in the chain has little influence on reduction potentials. Isopropenylacetylene is the compound most easily reduced. Increased length of the chain of the radical attached to the triple bonds results in some lowering of the half-wave potential. Substitution of an ethyl group by vinyl has no appreciable effect. Increase in length and branching of a radical attached to the double bond leads to a somewhat increased half-wave potential. Introduction of a second methyl group at the double bond has little effect on the potential. If, however, one methyl group substitutes the acetylenic hydrogen and another an ethylenic hydrogen, the potential is sharply increased (up to 2.8 eV).

The above peculiarities in the polarography of vinylacetylenic hydrocarbons can be most easily explained by the effect of the radicals on the adsorption of hydrocarbons by the mercury surface, without which the reduction is impossible.

III. CHEMICAL PROPERTIES OF ENYNE HYDROCARBONS

The chemical reactions of enyne hydrocarbons usually fall into two groups, determined either by multiple bonds, particularly by the conjugated vinylacetylenic system, or by the terminal acetylenic hydrogen atom. The first group includes additions, complex formations, homo- and heterocyclisations, and polymerisations. The second group covers substitutions of hydrogen by halogens, metals, and other elements, as well as condensations with carbonyl compounds.

A. REACTIONS OF MULTIPLE BONDS

1. Action of Oxidising Agents

Gaseous vinylacetylene is not oxidised by atmospheric oxygen. In the liquid phase it easily forms peroxides which remain, after the evaporation of vinylacetylene, as a yellow, explosive residue. In the presence of 5% chloroprene the oxidation rate of vinylacetylene is increased 5–6 times; in the presence of water it is halved. In the presence of 0.5–1% Neozone D (phenyl-β-naphthylamine) or the antioxidant from wood resin the oxidation by atmospheric oxygen does not take place[245]. Vinylacetylene and its homologues containing a terminal ethynyl group are oxidised by atmospheric oxygen in the presence of CuCl + NH_4Cl according to the following scheme[246,247]:

$$2R{-}CH{=}CH{-}C{\equiv}CH \xrightarrow{O_2} R{-}CH{=}CH{-}C{\equiv}C{-}C{\equiv}C{-}CH{=}CH{-}R.$$

Ozone primarily attacks the double bond. Typical of this reaction is the ozonolysis of deca-2,8-diene-4,6-diyne to diacetylenedicarboxylic acid[247]:

$$CH_3{-}CH{=}CH{-}C{\equiv}C{-}C{\equiv}C{-}CH{=}CH{-}CH_3 \xrightarrow{O_3} HOCO{-}C{\equiv}C{-}C{\equiv}C{-}COOH$$

With vinylbutyl- and isopropenylacetylenes the ozonolysis rate changes after the addition of 1 mole of ozone[248].

Hydrogen peroxide in formic acid reacts with vinylacetylene at the double bond[249,250]:

$$HC{\equiv}C{-}CH{=}CH_2 \longrightarrow HC{\equiv}C{-}CHOH{-}CH_2OH.$$

The reaction with peracids also takes place primarily at the double bond. For instance, the oxidation of hex-1-en-3-yne by benzoyl hydroperoxide yields the oxide previously prepared from the bromohydrin[251]:

$$C_2H_5{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{C_6H_5CO{-}OOH} C_2H_5{-}C{\equiv}C{-}CH{-}CH_2$$

(O; KOH; HOBr) $\rightarrow C_2H_5{-}C{\equiv}C{-}CHOH{-}CH_2Br.$

Acetyl, benzoyl, and phthalyl hydroperoxides react in the same manner with the phenyl derivatives of vinylacetylenes and dienynes[77,78,99,247,252,253].

In order to determine their structure, enyne hydrocarbons have often been oxidised by potassium permanganate to acids[54]. Vinylacetylene has been used as fuel, for instance in welding[198]. There are several patents available on the subject[254,255].

2. Hydrogenation

Hydrogenation of vinylacetylene has for a long time attracted attention as a key factor in the possible preparation of butadiene from acetylene. The first results were published as far back as 1935, by Lebedev[256] and Klebanskii and collaborators[257,258]. Their results, as well as those of the Japanese chemists[259,261], showed that hydrogenation of vinylacetylene over different palladium, platinum, and nickel catalysts yields a mixture of butadiene and the products of further hydrogenation. The yield of butadiene did not exceed 75–78% of the reacted acetylene. Neither ethylacetylene nor methylallene were observed in the mixture. The only strictly selective processes discovered were the electrochemical hydrogenation in weakly alkaline media at platinum electrodes, and reduction by means of $CrCl_2$.

Klebanskii et al.[262] attempted recently to improve the selectivity of the process, and develop an industrial method for the preparation of butadiene from vinylacetylene. On the basis of the data available in the literature and from their own results, they chose as catalyst palladium on silica gel. According to them the initial stage of the reaction is zero order with respect to vinylacetylene, and first order with respect to hydrogen. The apparent activation energy was ~ 10 000 cal/mole. Hydrogenation was practically selective up to 30%, the yield of butadiene being 90–95% with respect to reacted vinylacetylene. Later the hydrogenation of butadiene formed in the reaction began. Changes in catalyst carriers and solvents affected the hydrogenation rate, but not the selectivity. The latter is increased somewhat by the increase in temperature and rate of agitation, and is higher in neutral and acid than in alkaline media. The addition of catalyst poisons (H_2S, mercury and copper salts) lowers the selectivity. On the other hand, the addition of lead or copper acetates increases it[263].

Catalytic hydrogenation of vinylacetylene has been covered by many patents. Of special interest are those in which vinylacetylene is hydrogenated to butene and butanes in 87% yield. The mixtures obtained can be used to prepare 2,2,4-trimethylpentane (isooctane)[264,265]. There are patents on several reductions by nascent hydrogen, e.g. by means of zinc powder and alkali[266–268], potassium amalgam[269], etc. In the hydrogenation by the latter method some methylallene is formed. The formation of methylallene is also observed in catalytic hydrogenations under pressure over catalysts containing iron[270].

In the presence of catalysts vinylacetylene homologues can also add hydrogen selectively to their triple bond, but the process is to a greater or less extent followed by further hydrogenation of the dienes to olefines[92,271–273]. Alkenyl- and isoalkenylacetylenes, as well as their aromatic analogues, give dienes in good yields by hydrogenation over colloidal palladium. Under the same conditions the hydrogenation of vinylalkyl- and vinylarylacetylenes cannot be used as a preparative method for obtaining dienes, the latter being to a considerable extent simultaneously hydrogenated to olefines *. Hydrogenation of enyne hydrocarbons to dienes can be carried out over an iron catalyst under pressure[72,274]. Data are available on the exhaustive hydrogenation of enyne hydrocarbons to paraffins[28,52].

3. Addition of Halogens

The reaction of enyne hydrocarbons with fluorine has not been studied. Thermal and photochemical chlorination of vinylacetylene have been studied in the gaseous phase at 60°—150° and 650 mm Hg. At ordinary temperatures polymerisation occurs extensively, whereas at higher temperatures mainly tetrachlorides are formed. In chlorinations under pressure explosions with the separation of carbon were observed. Chlorination at 120° gave a dichloride of b.pt. 35° (40 mm Hg), namely 1,2-dichloro-buta-1,3-diene[275]

The chlorination of vinylacetylene in very dilute chloroform solution, at low temperatures (down to -60°) and with a deficiency of chlorine, can yield small quantities of dichlorides. All possible isomers are formed with allenic (III) and acetylenic (I) dichlorides predominating[45,276]:

$$H{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{Cl_2} \begin{cases} \rightarrow HC{\equiv}C{-}CHCl{-}CH_2Cl & (I) \\ \rightarrow CHCl{=}CCl{-}CH{=}CH_2 & (II) \\ \rightarrow CHCl{=}C{=}CH{-}CH_2Cl & (III). \end{cases}$$

During the chlorination of vinylethylacetylene large quantities of high-boiling products are formed. Nevertheless, the acetylenic dichloride, containing small quantities of 1,3-diene dichloride, predominates in the mixture. 1,4--Addition does not take place.

Bromination of vinylacetylene in chloroform solution[277] gives good yields of dibromides. As in chlorination, all possible isomers are formed, with allenes and dienes predominating. The relative yield of allenic dibromide is increased by lowering the temperature[278]. It seems that the dienic dibromide is formed partly by isomerisation of the allenic product. The nature of bromine addition to vinylacetylene homologues depends on the structure of the compounds involved. Non-conjugated enyne hydrocarbons and vinylalkynes add bromine exclusively to their double bond[43,166,279,280]:

$$CH_3{-}C{\equiv}C{-}CH_2{-}CH{=}CH_2 \xrightarrow{Br_2} CH_3{-}C{\equiv}C{-}CH_2{-}CHBr{-}CH_2Br,$$

$$CH_3{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{Br_2} CH_3{-}C{\equiv}C{-}CHBr{-}CH_2Br.$$

Isopropenylacetylene also adds bromine[281]. Alkenylacetylenes yield primarily allenic dibromides with small quantities of 1,3-dienic dibromides. Acetylenic dibromides are not formed at all[281,282].

$$CH_3{-}CH{=}CH{-}C{=}CH \xrightarrow{Br_2} CH_3{-}CHBr{-}CH{=}C{=}CHBr.$$

In all cases allenic and acetylenic dibromides are easily isomerised to 1,3-diene dibromides under the influence of CuBr and HBr. The preparation of tetrabromides from enyne hydrocarbons has been achieved repeatedly[2,28,29,52,43,166,275,277].

The addition of iodine to enyne hydrocarbons with isolated multiple bonds leads to both possible diiodides, together with the tetraiodides[283]. Vinylacetylenic hydrocarbons add iodine primarily to their triple bond, regardless of structure. The reaction only proceeds in light[283,284]. Their reaction with interhalogen compounds has also been studied. Iodine monochloride adds in the same way as bromine, but the action of iodine monobromide resembles more that of iodine[45].

Analogous behaviour is observed in the additions of halogens to vinylacetylenic alcohols and esters[285,286].

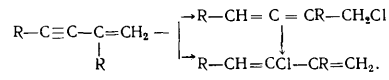
4. Addition of Hydrogen Halides

The reaction of vinylacetylenic hydrocarbons with hydrogen halides has been studied thoroughly, as it is involved in the production of such valuable synthetic rubber monomers as chloroprene and fluoroprene[287]. Hydrogen fluoride unites with vinylacetylene and isopropenylacetylene at the 1,2-position in the presence of mercury compounds, yielding fluoroprene. Another molecule of hydrogen fluoride adds at the same position[288–291]:

$$HC{\equiv}C{-}CH{=}CH_2 \xrightarrow{HF} CH_2{=}CF{-}CH{=}CH_2 \xrightarrow{HF} CH_3{-}CF_2{-}CH{=}CH_2.$$

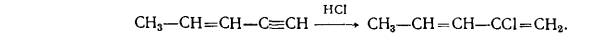
* It should be noted that in the hydrogenation of ethynylcyclohexene over Pd/Ni, vinylcyclohexene was obtained only in 12% yield[476], but in the hydrogenation over colloidal palladium or $Pd/CaCO_3$ the yields were good[92,220].

Without a catalyst, hydrogen chloride and bromide react with vinylacetylene, and alkenyl-, and isoalkenylacetylenes at 1,4- and 1,2- positions [71,292,293]. In the presence of catalysts only 1,2- addition products are obtained [71,73,178,294-301]:



In the case of ethylvinyl- and isopropenylacetylenes hydrogen bromide reacts also with the ethylenic bonds, but yields of these products are small [302]. The second molecule of hydrogen halide is added at 1,4-position, yielding, in the case of vinylacetylene, 1,3-dihalogeno-but-2-enes.

In contrast to the above hydrocarbons, alkenylacetylenes add hydrogen chloride and bromide at 1,2- or 1,4-positions in the absence of catalysts [302,303]:



Enyne hydrocarbons with isolated multiple bonds add hydrogen halides to the triple bond [166,279].

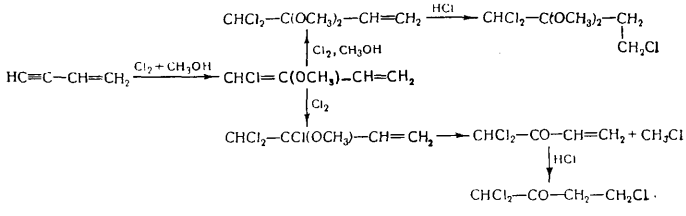
Thus, in all cases, regardless of the structure of the enyne hydrocarbon, the addition of the proton attacking the molecule occurs exclusively, or almost exclusively, at the acetylenic bond. The position of attachment of the anion depends on the structure of the hydrocarbon and reaction conditions. It seems that hydrohalogenation proceeds via a π-complex.

Hydrochlorination and hydrofluorination of vinylacetylene are described in a large number of papers and patents [287]. A method has been devised for separating diacetylene from vinylacetylene by removing the latter in the form of chloroprene after reaction with HCl [304].

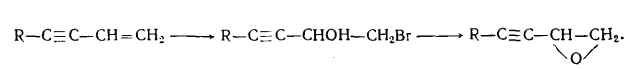
5. Addition of Hypohalogenous Acids and Esters

The reaction of vinylacetylene with halogeno-amides in aqueous and alcoholic solutions yields a complex mixture of products. As with the addition of hypohalogenites, substitution of the acetylenic hydrogen by halogen occurs, the compound obtained subsequently reacts further with hypohalogenites [305].

The action of chlorine on methanolic vinylacetylene gave a small yield of impure 1-chloro-2-methoxybuta-1,3--diene and a series of products of its subsequent transformations [306]:

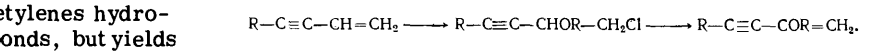


Addition of hypobromous acid to vinylalkylacetylenes by means of bromoacetamide in aqueous solution gave only the product of addition of HOBr at the double bond [307]:



Acetylonic epoxides were prepared from such addition products.

The reaction of benzenedichloro- and benzenedibromosulphonamides with ethanolic solutions of vinylalkylacetylenes also leads to the addition of alkylhypohalogenites at the double bond only. The acetylenic β-bromo-ethers thus obtained give alkoxyvinylacetylenes on dehydrohalogenation [305,308]:

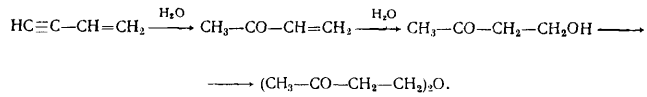


Thus, it was established that, like bromine, hypobromous acid and its esters are added at the double bond of vinylalkynes. This type of addition was explained by the shift of electron density in the hydrocarbons towards the double bond under the influence of substituents.

Dialkenylacetylenic hydrocarbons add hypobromites at at the double bond. Thus in the case of vinylisopropenylacetylene the addition takes place at the isopropenyl group Vinylalkynols behave similarly with respect to hypoiodites [309]. Enyne hydrocarbons with non-conjugated bonds also add hypobromites primarily to the ethylenic bond, but with a smaller selectivity [166].

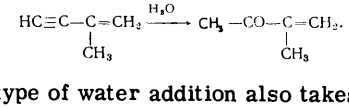
6. Addition of Water, Alcohols, Acids, and Phenols

The reaction of vinylacetylene with water in the presence of Kucherov's catalyst gives good yields of methyl vinyl ketone. A number of papers and patents are devoted to the development of this method. The by-products in the reaction are 3-oxobutanol and 3-oxobutyl ether [310]:



Some patents claim the formation of diacetyl in this reaction [311,312]. In the presence of the same catalyst, and in solution of different alchols, vinylacetylene yields methyl β-alkoxyethyl ketones; in phenol solution, methyl β-phenoxyethyl ketone is formed and, in solutions of organic acids, methyl β-acyloxyethyl ketones [313-315].

Methyl vinyl ketone can be prepared by the hydration of vinylacetylene in the gaseous phase at 325°–400° over cadmium tungstate, zinc oxide, or cadmium calcium phosphate catalysts. The first catalyst is the most active: at 325° and in the presence of ten times the theoretical amount of steam it gives methyl vinyl ketone in 87% yield. The by-products in this reaction are the dimer of methyl vinyl ketone (2-acetyl-6-methyl-2,3-dihydropyran) and vinylacetylene polymers [316]. Vinylacetylene homologues containing a terminal vinylethynyl group can also be hydrated to corresponding ketones. Aldehydes were not observed in any of the reactions [56,121,317-320].



The same type of water addition also takes place in hydrations by means of $HgSO_4$ in alcoholic solutions [314], in the presence of mercuric acetate in acetic acid [319] and by means of 80% formic acid [320]. The addition of water to this type of enyne therefore strictly obeys Markownikoff's rule.

Hydration of vinylalkynes under the conditions of Kucherov's reaction[321,322], as well as in the gaseous phase over cadmium calcium phosphate catalyst[323] takes a different couse: oxygen is added primarily not to the middle, but to a terminal atom of the conjugated system, and the alkyl allyl ketones (I) formed are isomerised in acid media to alkyl propenyl ketones (II).

$$R-C\equiv C-CH=CH_2 \xrightarrow{H_2O} \underset{(I)}{R-CO-CH_2-CH=CH_2} \xrightarrow{[H^+]} \underset{(II)}{R-CO-CH=CH-CH_3}.$$

Such hydration could be explained by 1,4-addition of water. However, it also takes place in the case of non-conjugated enynes, e.g. methylallylacetylene, where 1,4-addition is not possible[324,325].

$$CH_3-C\equiv C-CH_2-CH=CH_2 \xrightarrow{H_2O} \begin{cases} CH_3-CO-CH_2-CH_2-CH=CH_2\ (85\%) \\ CH_3-CH_2-CO-CH_2-CH=CH_2 \\ \downarrow \\ CH_3-CH_2-CO-CH=CH-CH_3\ (15\%). \end{cases}$$

Water is added to the acetates of the corresponding alcohols[326] in the same way as to the vinylalkynes. The ethers from such alcohols, however, form methoxyalkyl vinyl ketones after the addition of water[327]. Chlorides, alcohols, ethers, esters, and amines of the type $R-C\equiv C-CH_2X$ form, by hydration, only ketones of the type $R-CO-CH_2-CH_2X$ [326-330]. This behaviour is complicated by the fact that, quite unexpectedly, isopropenylalkynes are hydrated, in 90% yield, in the opposite sense, i.e. they behave like isopropenylacetylene itself:

$$\underset{\substack{|\\CH_3\\(V)}}{CH_3-C\equiv C-C=CH_2} \xrightarrow{H_2O} \underset{\substack{|\\CH_3}}{CH_3-CH_2-CO-C=CH_2}.$$

Similarly, the hydration of vinylisopropenylacetylene yields only propenyl isopropenyl ketone[332]:

$$\underset{\substack{|\\CH_3}}{CH_2=C-C\equiv C-CH=CH_2} \xrightarrow{H_2O} \underset{\substack{|\\CH_3}}{CH_2=C-CO-CH_2-CH=CH_2} \xrightarrow{[H^+]}$$

$$\longrightarrow \underset{\substack{|\\CH_3}}{CH_2=C-CO-CH=CH-CH_3}.$$

Oxygen is, therefore, always linked to the most substituted carbon atom.

Hydration rules for vinylacetylenic hydrocarbons do not seem to be connected with electron shifts within the molecules under the influence of substituents (see formula on p. 495). Such shifts occur in opposite directions in hydrocarbons of types (II) and (III), and yet they add water in the same way. In hydrocarbons (IV) and (V) the electron cloud shifts in the same direction under the influence of substituents, yet water adds in a different way to the two compounds. For the unsymmetrically disubstituted acetylenes of type $CH_3-C\equiv C-R$, where $R = C_2H_5$, $CH(CH_3)_2$, and $C(CH_3)_3$, significantly non random addition is observed only in the last case, where a mixture of ketones, containing 65% of ethyl t-butyl ketone, is formed[333].

It seems that for all cases the sense of the addition is determined by the ease of formation and stability of the intermediate complex formed in the presence of the catalyst. It therefore depends on steric and other factors besides the polarisation of the initial molecule.

Alcohols are added to both multiple bonds of vinylacetylene in the presence of boron trifluoride and red mercuric oxide[334-336]:

$$HC\equiv C-CH=CH_2 \xrightarrow{ROH} CH_3-C(OR)_2-CH_2-CH_2-OR.$$

Glycols are added in the same way[337]. In the presence of alkali, different products are obtained, depending on the conditions[338,339]. In the presence of potassium alcoholate, at ordinary pressures, alcohols are added at 1,4-positions, yielding α-alkoxybutadienes, after isomerisation of the allene, formed initially to 1,3-diene[339,340].

$$HC\equiv C-CH=CH_2 \longrightarrow CH_2=C=CH-CH_2OR \longrightarrow CH_2=CH-CH=CH-OR.$$

β-Alkoxybutadienes, and, sometimes, acetylenic ethers are obtained as by-products in this reaction. If the reaction is carried out in the presence of sodium alcoholates, and under pressure, the 1,4-addition is followed by the isomerisation of the allenic ether first formed to an acetylenic ether[341]:

$$HC\equiv C-CH=CH_2 \xrightarrow{ROH} CH_2=C=CH-CH_2OR \longrightarrow CH_3-C\equiv C-CH_2-OR.$$

Addition of alcohols to vinylacetylene homologues containing a terminal ethynyl group proceeds in the same way as the addition of water[342,343]:

$$\underset{\substack{|\\CH_3}}{HC\equiv C-C=CH_2} \xrightarrow{CH_3OH} \underset{\substack{|\\CH_3}}{CH_3-C(OCH_3)_2-C=CH_2} \xrightarrow{CH_3OH} \underset{\substack{|\\CH_3}}{CH_3-C(OCH_3)_2-CH-CH_2OCH_3}.$$

With cyclic conjugated enynes, the reaction is complicated by the formation of dimers of dienic ethers[344,345]. Enyne hydrocarbons with isolated multiple bonds add alcohols in the presence of $BF_3.HgO$ only to their acetylenic bond. The double bond does not react[346]. According to some authors vinylalkynes add alcohols in a similar manner in the presence of acid catalysts (boron trifluoride)[336,346]. However in the light of the latest results on the addition of water and alcohols to vinylalkynes in the presence of alcoholates, such claims need verifying. Vinylalkynes add alcohols (in the presence of sodium alcoholates) and water in an analogous manner[347]:

$$CH_3-C\equiv C-CH=CH_2 \xrightarrow{CH_3OH} CH_3-COCH_3=CH-CH=CH_2.$$

In the case of vinylethylacetylene a mixture of two ethers is formed, which on hydrolysis yields the same ethyl propenyl ketone[347]:

$$CH_3-CH_2-C\equiv C-CH=CH_2 \rightarrow$$

$$\rightarrow \begin{cases} CH_3-CH_2-COCH_3=CH-CH=CH_2 \\ \downarrow \\ CH_3-CH=COCH_3-CH=CH-CH_3 \end{cases} \rightarrow C_2H_5-CO-CH=CH-CH_3.$$

Allylacetylenes add alcohols similarly[346]:

$$R-C\equiv C-CH_2-CH=CH_2 \xrightarrow{ROH} R-C(OR)_2-CH_2-CH_2-CH=CH_2.$$

Acids unite with vinylacetylene to form β-acyloxybutadienes only, according to the scheme[348-350]

$$H-C\equiv C-CH=CH_2 \xrightarrow{RCOOH} CH_2=C(OCOR)-CH=CH_2.$$

In the presence of a catalyst based on boron trifluoride, 60% formyloxybutadiene, and 30% acetoxybutadiene are

formed. Poorer results are however obtained with mercuric sulphate. Benzoic acid did not react with vinylacetylene. A patent claims the preparation of β-phenoxybutadiene from vinylacetylene and phenol[351].

The behaviour of vinylacetylenic hydrocarbons in their reactions with water, alcohols, and hydrogen halides is of considerable interest to theoretical organic chemistry, particularly as regards the determination of the mechanism of Kucherov's reaction.

7. Addition of Sulphur, Nitrogen, Phosphorus, and Silicon Compounds

Vinylacetylene adds mercaptans to the double bond only and that in the opposite sense to Markownikoff's rule. It seems that a radical mechanism is operative in this reaction[352]:

$$HC\equiv C-CH=CH_2 \xrightarrow{CH_3C_6H_4SH} CH\equiv C-CH_2-CH_2SC_6H_4CH_3.$$

According to one patent[353] vinylacetylene reacts with hydrogen sulphide at 200° in the presence of Co_2S_3. Vinylacetylene adds thiocyanic acid at 50° in the presence of HgO giving thiocyanobutadiene[354]:

$$HC\equiv C-CH=CH_2 \xrightarrow{HSCN} CH_2=C(SCN)-CH=CH_2.$$

Vinylacetylene adds secondary amines at 1,4-positions, on heating under pressure in aqueous solution, yielding allenic amines; by prolonged heating with an excess of initial amine, or by the action of alcoholates, these are transformed into acetylenic amines[355]:

$$HC\equiv C-CH=CH_2 \xrightarrow{R_2NH} CH_2=C=CH-CH_2NR_2 \rightarrow CH_3-C\equiv C-CH_2NR_2.$$

It should be noted that diacetylene unites with amines even without heating[356], whereas this reaction is not characteristic of butadiene[357]. According to patents, vinylacetylene reacts with ammonia in the presence of a catalyst (Pb–Cd), yielding aliphatic amines as well as collidine and picoline[358]. Addition products are also formed with secondary amines – piperidine, morpholine, and methylaniline – in the presence of copper compounds[359].

Whereas amines do not react with vinylakynes on heating to 120° under pressure, they do react with analogous alcohols under such conditions. Allenic amino-alcohols are formed at first, but they are subsequently isomerised to aminoalkynols[360,361]. The addition products of amines with vinylacetylenic hydrocarbons can be obtained without heating by the recently discovered reaction of vinylacetylenic hydrocarbons with lithium dialkylamides. By treating with water the addition products of lithium dialkylamides with vinylacetylene, acetylenic amines are obtained. Such products obtained with vinylalkynes yield allenic amines on treatment with water[362].

$$HC\equiv C-CH=CH_2 \xrightarrow{R_2N-Li} H-C(Li)=C=CH-CH_2NR_2 \rightarrow Li-C\equiv C-CH_2-CH_2NR_2 \rightarrow$$
$$\xrightarrow{H_2O} HC\equiv C-CH_2-CH_2NR_2,$$

$$R-C\equiv C-CH=CH_2 \xrightarrow{R_2N-Li} R-CLi=C=CH-CH_2NR_2 \xrightarrow{H_2O} R-CH=C=CH-CH_2NR_2.$$

An exception is vinylmethylacetylene, which, under such reaction conditions mainly yields the dimer.

Similarly to lithium dialkylamides, lithium dialkylphosphides are added easily to vinylalkynes, yielding allenic phosphines[363]:

$$C_2H_5-C\equiv C-CH=CH_2 \xrightarrow{LiPR_2} C_2H_5-CLi=C=CH-CH_2PR_2 \xrightarrow{H_2O}$$
$$\rightarrow C_2H_5-CH=C=CH-CH_2PR_2.$$

In contrast to lithium phosphides, phosphorus tri- and pentachlorides react with the triple bond in vinylacetylene and its homologues[364–366]:

$$HC\equiv C-CH=CH_2 \xrightarrow{PCl_3,\ O_2} Cl_2PO-CH=CCl-CH=CH_2,$$

$$C_2H_5-C\equiv C-CH=CH_2 \xrightarrow{PCl_5} Cl_4P-\underset{\displaystyle C_2H_5}{\underset{|}{C}}=CCl-CH=CH_2 \xrightarrow{SO_2} Cl_2PO-\underset{\displaystyle C_2H_5}{\underset{|}{C}}=CCl-CH=CH_2.$$

In the reaction of vinylacetylene and isopropenylacetylene with phosphorus pentachloride simultaneous substitution of one of the hydrogen atoms by chlorine takes place[365].

Silanes also react with the vinylacetylene triple bond[367]. The catalyst for this interesting reaction is H_2PtCl_6.

$$HC\equiv C-CH=CH_2 \xrightarrow{Cl_2SiHR} Cl_2RSi-CH=CH-CH=CH_2.$$

8. Additions Resulting in the Lengthening of the Carbon Chain

Reactions belonging to this group are those with (a) acetylenes, (b) free radicals, (c) organolithium compounds, (d) halogen derivatives, (e) hydrocyanic acid, (f) nickel carbonyls, (g) dialkylcarbonates, and (h) diazo compounds.

(a) During its preparation from acetylene vinylacetylene can add another acetylene molecule and give ethynylbutadiene. At the same time the addition of vinylacetylene to acetylene takes place, forming divinylacetylene[368]:

$$HC\equiv C-CH=CH_2 \xrightarrow{HC\equiv CH} \begin{cases} HC\equiv C-CH=CH-CH=CH_2 \\ CH_2=C-C\equiv C-CH=CH_2. \end{cases}$$

(b) Triphenylchloromethane and mercury in benzene solution reacted for 12 days with vinylacetylene to yield apparently the 1,4-addition product of free triphenylmethyl radicals and vinylacetylene[369].

(c) Lithium alkyls and lithium aryls can react with vinylalkynes even at -60°. By treating the adducts with water, good yields of allenic hydrocarbons are obtained[370–372]:

$$CH_3-C\equiv C-CH=CH_2 \xrightarrow{C_4H_9-Li} CH_3-CLi=C=CH-CH_2-C_4H_9 \xrightarrow{H_2O}$$
$$\rightarrow CH_3-CH=C=CH-CH_2-C_4H_9.$$

Large yields of allenic hydrocarbons in this reaction seem to be connected with the low reactivity of intermediate addition products, containing lithium attached to the double bond.

(d) In the presence of Gustavson's catalysts vinylacetylene and its homologues containing a terminal ethynyl group add tertiary halogen derivatives to their triple bond[373,374]:

$$HC\equiv C-CH=CH_2 \xrightarrow{R_3C-Cl} R_3C-CH=CCl-CH=CH_2.$$

Under the same reaction conditions vinylalkynes yield primarily allenic adducts, radical adding to the double bond[375]:

$$R{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{R_3C-Cl} R{-}CCl{=}C{=}CH{-}CH_2{-}CR_3.$$

Thus, only in the first case is the sense of the addition of halogen derivatives identical with that of hydrogen halides in the presence of catalysts.

Vinylacetylene adds α-chloro-ethers in the presence of $BiCl_3$, primarily at 1,4-position. However, the primary addition products can be isomerised to compounds with conjugated multiple bonds[376]:

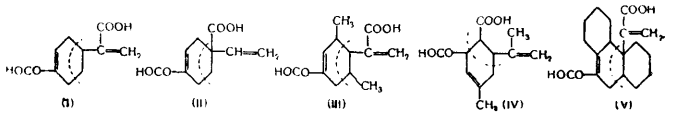
$$HC{\equiv}C{-}CH{=}CH_2 \xrightarrow{ROCH_2Cl} \begin{cases} RO{-}CH_2{-}CH{=}C{=}CH{-}CH_2Cl \\ \downarrow \\ RO{-}CH_2{-}CH{=}CCl{-}CH{=}CH_2. \end{cases}$$

Acid chlorides unite with vinylacetylene giving dienic β-chloro-ketones[377].

(e) The reaction of vinylacetylene with hydrocyanic acid has only been described in one patent, which claims that the reaction at 50°, in the presence of copper powder, yields 1-cyanobuta-1,3-diene[378]:

$$HC{\equiv}C{-}CH{=}CH_2 \xrightarrow{HCN} NC{-}CH{=}CH{-}CH{=}CH_2.$$

(f) Of considerable interest is the reaction of vinylacetylene and its homologues with nickel carbonyls. This yields the dimers of the expected 1,3-dienoic acids. Reactions of nickel carbonyl with vinylpropenyl-, isopropenyl- and cyclohexenyl acetylenes have been studied[379-382]. There are contradictions among the available data regarding the structure of the intermediate 1,3-dienoic acids and the course of their dimerisation. Intermediate dienoic acids were attributed formulae of the type R–CH = CR'–CH = CH–COOH or R–CH = CR'–C(COOH) = CH_2. Authors who agree on the structure of dienoic acids nevertheless have different views on the dimerisation mechanism. For instance, two formulae, (I) and (II), were suggested for the dimeric acid from vinylacetylene[381,382]. Formula (II) seems to be better justified, having been verified by synthesis[381]. Acids prepared from propenyl-, isopropenyl- and cyclohexenylacetylenes were given formulae (III), (IV), and (V):



Further study is needed to determine conclusively the structure of all these adducts.

(g) By prolonged heating of isopropenylacetylene with diethyl carbonate in the presence of sodium alcoholate, addition to the triple bond takes place[383]:

$$HC{\equiv}C{-}C(CH_3){=}CH_2 \xrightarrow{(C_2H_5O)_2CO} \begin{cases} C_2H_5OCO{-}CH_2{-}C(OC_2H_5)_2{-}C(CH_3){=}CH_2 \\ C_2H_5OCO{-}CH{=}COC_2H_5{-}C(CH_3){=}CH_2. \end{cases}$$

(h) Diazomethane reacts with the triple bond in vinylacetylene yielding ethynylpyrazoline[384].

$$HC{\equiv}C{-}CH{=}CH_2 + CH_2N_2 \rightarrow HC{\equiv}C{-}C(=N{-}NH){-}CH_2.$$

Dombrovskii has shown that aromatic diazonium halides halogenate and arylate the vinylacetylene double bond[385-387]:

$$HC{\equiv}C{-}CH{=}CH_2 \xrightarrow{C_6H_5N_2Cl} HC{\equiv}C{-}CHCl{-}CH_2{-}C_6H_5.$$

Considerable quantities of allenic chlorides (1,4-addition[388]) are also formed in the reaction.

9. Isomerisation with Rearrangement of the Multiple Bonds

Several cases have been described of isomerisation by multiple bond migration during the preparation of enyne hydrocarbons. Such isomerisation may result in the formation of a conjugated system from the non-conjugated one, as, for instance, in the case of allylacetylene formed in the reaction of allyl bromide with sodium acetylide[167]. In other cases the migration of the entire system of multiple bonds takes place. For example, an excess of sodium amide causes the isomerisation of methylisopropenylacetylene during its preparation according to the scheme[180]

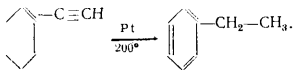
$$NaC{\equiv}C{-}C(CH_3){=}CH_2 \xrightarrow{CH_3Br} CH_3{-}C{\equiv}C{-}C(CH_3){=}CH_2 \xrightarrow{NaNH_2} HC{\equiv}C{-}CH{=}C(CH_3)_2.$$

When the reaction can yield two types of vinylacetylenes, namely R–C ≡ C–CH = CH_2 and R–CH = CH–C ≡ CH, the first compound usually predominates[20,22].

Multiple bond migration is observed in brominating allylbutylacetylene with bromosuccinimide[389]:

$$C_4H_9{-}C{\equiv}C{-}CH_2{-}CH{=}CH_2 \longrightarrow C_4H_9{-}C{\equiv}C{-}CH{=}CH{-}CH_2Br.$$

Irreversible (Zelinskii') catalytic conversion is characteristic of alicyclic vinylacetylenes[390]

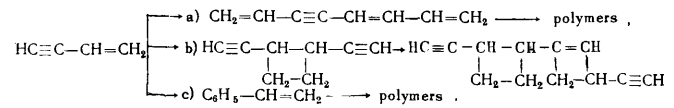


10. Dimerisation and Polymerisation of Vinylacetylene and its Homologues

Condensation reactions, characteristic of dienic hydrocarbons, can proceed in two ways — to form cyclic six-membered dimers, or linear polymers[356]. Vinylacetylenic hydrocarbons have a very small tendency to form six-membered rings. By dimerisation, they yield compounds containing four-membered rings[391]

Polymerisation of vinylacetylene at moderate temperatures and pressures can take three different paths, depending on the conditions, and yield (a) a linear dimer and its polymers, (b) a dimer with a four-membered ring and its

polymers, and (c) styrene and its polymers[1,391]:



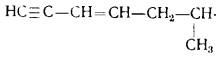
Linear dimerisation of vinylacetylene occurs under the action of the CuCl.NH_4Cl complex. The reaction mechanism is analogous to that for the formation of vinylacetylene[395]. Heating vinylacetylene without a catalyst at 105° yields a mixture of products containing 1% of dimer, 3% of trimer, 16% of tetramer, 8% of pentamer, and 72% of higher polymers. All the products contain four-membered rings[391].

Polymerisation of vinylacetylene to styrene is catalysed by organic acids. For instance, in the presence of acetic acid the yield of styrene can reach 50% of the reacted vinylacetylene[391]. Attempts have been made to determine the rate of dimerisation of vinylacetylene[396].

Slobodin studied the copolymerisation of vinylacetylene with SO_2. In the absence of water a polymer of the composition $(C_4H_4.SO_2)_x$ is formed, insoluble in water and organic solvents. In the presence of water the polymer has the composition $(C_4H_4.SO_3)_x$. In contrast to the case with butadiene sulphone monomer is not obtained in this reaction[397]

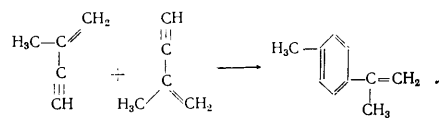
Possible preparations of valuable products, by copolymerisation of vinylacetylene, especially with dienes, have been covered by a number of patents[142,398-406]. The addition of vinylacetylene does not affect the rate of emulsion polymerisation of butadiene, but it does promote the cross-linking of chains in rubber, thus lowering its solubility and tensile strength. Vinylacetylene inhibits the polymerisation of butadiene by alkali metals[407]. The presence of small quantities of vinylacetylene in butadiene has a considerable effect on the toughness of butadiene-styrene rubbers[480]. Vinylacetylene does not affect the induction period of the polymerisation of vinylacetate in the presence of peroxides, but it somewhat inhibits the process[409]. It also retards the polymerisation of chloroprene and causes brittleness of the polymer[410]. Vinylacetylenes are recommended for stabilising chlorinated hydrocarbons and other products[411,412].

The polymerisation of vinylacetylene homologues has received even less attention. Linear dimerisation was only observed in the reaction of vinylmethylacetylene with lithium dialkylamides. The dimer obtained was shown to have the following structure[362]:



It seems that in this reaction lithium methylvinylacetylene, first formed by substituting a hydrogen atom in methylvinylacetylene, subsequently combines with the original hydrocarbon.

Prolonged heating of isoalkenylacetylenes in alcoholic solution, especially in the presence of acetic acid, yields dimers with six-membered rings. The structure of the main fraction of the dimers was established by oxidation to the corresponding aromatic acids[58,74,413]:

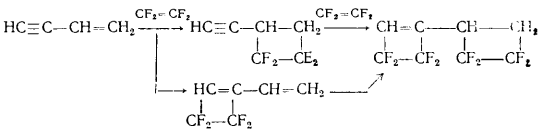


Analogous dimers are often formed during the dehydration of dialkylpropargyl alcohols. The presence of branched radicals at the terminal carbon of the double bond favours dimerisation[74]. In some cases the formation of dimers with eight-membered rings was observed. There are patents on the polymerisation of vinylmethyl- and isopropenylacetylene[414-416].

Heating at 300° for 24 h transforms vinylacetylene in 94% yield to a yellow powder, which chars above 300°[392]. At 25° and 6000 atm 50% of vinylacetylene polymerises in 350 h, and of butadiene in 280 h[393]. Heating vinylacetylene to 345°–355° with copper oxide yields a cuprenelike product[394]. Polymerisation to a solid product is also observed on irradiation by α-rays from radon[188]. Copolymerisation of isopropenylacetylene with SO_2 yielded similar products to those obtained from vinylacetylene[397].

11. Addition of Fluoroolefines.

Vinylacetylene reacts at 100° with tetrafluoroethylene forming cyclobutane and cyclobutene derivatives[417]:



12. Formation of Complexes

Very little is known of the reactions of vinylacetylenic hydrocarbons with the the salts of heavy metals with the exception of copper salts.

Solid cuprous chloride absorbs vinylacetylene; 1 g of salt absorbs 128 cm^3 of vinylacetylene, compared with 74 cm^3 of acetylene and 10 cm^3 of ethylene.

In solution vinylacetylene forms a complex with CuCl.NH_4Cl with the composition $C_4H_4.Cu_2Cl_2.NH_4Cl$.

In hydrochloric acid solution of CuCl the composition of the complexes formed depends on the acid concentration, e.g. CuCl.C_4H_4 (10% HCl) and 2CuCl.C_4H_4 (20% HCl). Dry HCl displaces vinylacetylene in the above complexes and the complex $C_4H_4.4CuCl.HCl$ is formed[420,421].

Vinylacetylene can displace carbon monoxide in cobalt carbonyl $Co_2(CO)_8$. With isopropenylacetylene, this carbonyl forms reddish brown crystals of composition $C_5H_8.Co_2(CO)_6$[422]. Complexes are probably also formed in the reaction of acetylenes and vinylacetylenes with palladium salts[423].

B. REACTIONS INVOLVING ACETYLENIC HYDROGEN

Metals, halogens, and, particularly, hydrocarbon radicals can be substituted for the acetylenic hydrogen in enyne hydrocarbons containing a terminal ethynyl group.

1. Substitution of Acetylenic Hydrogen by Halogens

Substitution of the acetylenic hydrogen by halogens takes place on passing vinylacetylene and its homologues containing a terminal ethynyl group through solutions of alkali

hypohalogenites. Chloro-, bromo-, and iodo-derivatives of vinyl-, propenyl-, and isopropenylacetylenes were prepared in this way[424-427]. They can also be prepared by dehydration of the corresponding tertiary acetylenic alcohols in the presence of formic acid[428].

$$HC\equiv C-CH=CH_2 \xrightarrow{NaOCl} Cl-C\equiv C-CH=CH_2$$

$$Cl-C\equiv C-\underset{\underset{CH_3}{|}}{COH}-CH_3 \xrightarrow{-H_2O} Cl-C\equiv C-\underset{\underset{CH_3}{|}}{C}=CH_2$$

Small quantities of acetylenic halides are also formed by the dehalogenation of vinylacetylenic dihalides[429]. Acetylenic halides have the interesting property of yielding unsaturated acids by reaction with alcoholic alkalis[430]:

$$R-CH=CR-C\equiv CCl \longrightarrow R'RC=CH-COOH.$$

2. Substitution of Acetylenic Hydrogen by Metals and Non-Metals

Vinylacetylenic hydrocarbons with a terminal ethynyl group have relatively labile ("acid") hydrogen atoms[431]. A study was made of the kinetics of the reaction of monosubstituted acetylenes with C_2H_5MgBr. If the reaction rate with butylacetylene is 100, that with isopropenylacetylene[432] is 40.

All alkenylacetylenes form the corresponding acetylides by the action of alkali amides in liquid ammonia. On reaction with solutions of organomagnesium compounds they displace saturated hydrocarbons yielding halogenomagnesiumacetylides, soluble in ether[433]. On treatment with alkaline solutions of silver and monovalent copper salts they form explosive acetylides[2,9,11,12,317,434,435], sometimes as double salts with those with which they reacted[11,12,434].

Crystalline mercury vinylacetylides have also been described[100,153,436,437]. Mercury bis(vinylacetylide) is formed in the reaction of vinylacetylene with alkaline solutions of K_2HgI_4 or mercuric acetate. At 60°–70° a product of the composition $C_{10}H_{12}O_7Hg_3$ is formed. Mercury derivatives can be used for separating and identifying geometrical isomers of vinylacetylenic hydrocarbons[100].

Organosilicon compounds containing vinylacetylenic radicals have been prepared by reacting alkylhalogenosilanes with bromomagnesiumvinylacetylides[438-440]:

$$R_3Si-Cl + BrMg-C\equiv C-CH=CH_2 \rightarrow R_3Si-C\equiv C-CH=CH_2.$$

Tin vinylacetylides were recently prepared by this method[441]:

$$R_3Sn-Cl + BrMg-C\equiv C-CH=CH_2 \rightarrow R_3Sn-C\equiv C-CH=CH_2.$$

3. Condensation with Carbonyl Compounds *

Vinylacetylene and its homologues containing a terminal ethynyl group can easily be condensed with various aldehydes, ketones, epoxides, acid anhydrides, and CO_2.

The reaction with formaldehyde can be carried out either by the Grignard-Iotsich method using vinylacetylene Grignard reagents[60,102,442] or by Reppe's method[443]:

$$HC\equiv C-CH=CH_2 + CH_2O \xrightarrow{[Cu(OCOH)_2]} CH_2OH-C\equiv C-CH=CH_2.$$

With other aldehydes, in addition to these two methods[444-446], condensations can also be carried out with sodium acetylide in liquid ammonia[447,448]. With unsaturated aldehydes, best results are obtained by using organomagnesium compounds[448,449].

Condensations of enyne hydrocarbons with ketones proceed easily by the Grignard-Iotsich reaction, using sodium amide in liquid ammonia or finely dispersed KOH in ether (Favorskii's method)[447,450-454]. Good results are obtained in condensations of vinylacetylenes or their metal derivatives in the presence of powdered KOH (according to Favorskii) with cyclic ketones[452,455-461], unsaturated ketones[462,463], hydroxy-[459], alkoxy-[464-466], and amino-ketones[467]. Nazarov and his collaborators carried out a large number of such condensations. Of special interest in this field is the condensation of isopropenylacetylene with β-ionone, as a step in the synthesis of carotenoid compounds[55,468,469]

In the reaction with epoxides halogenomagnesiumvinylacetylides yield primary alcohols[445]:

$$H_2C-CH_2 + BrMg-C\equiv C-CH=CH_2 \longrightarrow CH_2OH-CH_2-C\equiv C-CH=CH_2.$$
$$\quad\ O$$

With ethyl acetate, a tertiary alcohol containing two vinylacetylenic radicals[469] is formed:

$$CH_3-CO-OC_2H_5 + 2BrMg-C\equiv C-CH=CH_2 \longrightarrow CH_3-C(OH)(C\equiv C-CH=CH_2)_2.$$

Vinylacetylides react with acetic and other anhydrides yielding vinylacetylenic ketones[58,89,104,470].

$$(CH_3-CO)_2O + BrMg-C\equiv C-CH=CH_2 \rightarrow CH_3-CO-C\equiv C-CH=CH_2.$$

With carbon dioxide, sodium and magnesium derivatives of acetylene form enynoic acids, usually isolated as esters[371,471-473].

$$CO_2 + BrMg-C\equiv C-CH=CH_2 \rightarrow HO-CO-C\equiv C-CH=CH_2.$$

Heating vinylacetylene with paraformaldehyde and secondary amines results in the Michael condensation. This reaction is catalysed by ferric chloride[474,475]:

$$CH_2=CH-C\equiv CH + CH_2O + HNR_2 \rightarrow CH_2=CH-C\equiv C-CH_2NR_2.$$

4. Oxidative Condensation

In Section I the oxidative dimerisation of vinylacetylenes containing a terminal ethynyl group was considered. Similar oxidative condensation is possible between enyne hydrocarbons and other acetylenic compounds. Condensation of enynes with acetylenic acids has been used for the synthesis of natural higher unsaturated acids, for instance, erythrogenic acid[103,171]:

$$CH_2=CH(CH_2)_4-C\equiv CH + HC\equiv C-(CH_2)_7-COOH \xrightarrow{O_2,\ CuCl,\ NH_4Cl}$$

$$\rightarrow CH_2=CH-(CH_2)_4-C\equiv C-C\equiv C-(CH_2)_7-COOH.$$

* Vartanyan and his coworkers have recently shown that vinylacetylene can be condensed with aldehydes in the presence of KOH, provided the reaction is carried out without a solvent at very low temperatures[475].

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MOLECULAR SIEVES — PREPARATION, PROPERTIES, AND APPLICATIONS

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INTRODUCTION

The sorptive properties of sorbents depend chiefly on the area and chemical nature of the surface, the pore structure, and the distribution of effective pore radius.

The adsorption potential, which determines the amount of adsorption, can vary greatly with change in the geometrical shape of the internal surface; it is much greater in narrow pores and channels of molecular dimensions, owing to the superposition of the fields of the opposite walls, and this effect is more marked the finer the pores of the adsorbent[1]. The free adsorptive surface of an adsorbent also depends on the dimensions of the molecules of the substance being adsorbed, since some of the finest pores may be inaccessible to large molecules. This leads to the so-called ultraporosity effect.

Some sorbents are known to have pore diameters approximately equal to molecular dimensions. Only very small molecules can penetrate into these fine pores. McBain has called this phenomenon "persorption"[2].

Fine pores are also present in activated charcoal, silica gel, and other technical sorbents, so that each shows the ultraporosity effect to some extent. The surface area cal-

culated from the sorption isotherms for gases or dyes always depends on the dimensions of the molecules of the adsorbed substance.

Adsorbents with fine pores can be regarded as molecular sieves. The fact that the cross-sections of these pores are of molecular dimensions makes it possible to separate gaseous and liquid mixtures by making use of differences in the size and shape of the component molecules. Such sorbents can sift out molecules of different sizes (hence the name "molecular sieves")[3,4,5]. Examples include zeolites, Saran charcoal, porous glasses, etc.

Zeolites are aluminosilicate polyhydrates of general composition

$$(R'_2, R)O \cdot Al_2O_3 \cdot nSiO_2 \cdot mH_2O,$$

where R' is a univalent cation (Na^+, K^+, Li^+) and R a divalent cation (Ca^{2+}, Sr^{2+}, Ba^{2+}, etc.). If the water molecules are removed from the zeolite crystals, other substances can be adsorbed in their place.

The molecular-sieve properties of zeolites have been known since 1925 [2], when Weigel and Steinhoff[6] discovered that the mineral chabazite exhibits selective sorption. They found that the vapours of water, methyl and ethyl alcohols, and formic acid were adsorbed rapidly on chabazite but that those of acetone, ether, and benzene were not. However, natural zeolites have not been used for the separation of mixtures.

Other natural zeolites with molecular-sieve properties are known (faujasite, gmelinite, mordenite) but they occur only in rare and poor deposits.

In the past twenty years methods have been developed in other countries for the preparation of synthetic zeolites and they are now produced on a large scale by Linde Air Products (USA). In a review of sorption processes up to 1957 [7] it was noted that the introduction of synthetic molecular sieves for practical purposes was one of the most important achievements in the application of adsorption in the preceding decade.

The industrial production of molecular sieves was preceded by extensive research, particularly in England by Barrer and his school. Barrer is the author of the first patents on the preparation of synthetic zeolites and their use for the separation of mixtures.

THE STRUCTURE AND COMPOSITION OF ZEOLITES. CLASSIFICATION

Like many silicates, zeolites are made up of SiO_4^{4-} tetrahedra, which are cross-linked via common O^{2-} ions to form complex anionic radicals[8,9]. In the aluminosilicates some of the Si^{4+} ions are replaced by Al^{3+} ions, so that the lattice has a residual negative charge. The cations neutralising this charge in the anionic framework are situated in the internal spaces in the lattice, and this gives the zeolites ion-exchange properties[10]. The cations in the zeolite lattices usually have a large ionic radius and low charge, for example Na^+, K^+, Ca^{2+}, Ba^{2+}, and less frequently, Rb^+ and Cs^+. The Al:Si ratio in the lattice is variable but one univalent cation is present for every Al^{3+} ion, to neutralise the excess negative charge.

The structure of the zeolite crystal is determined by the magnitude of the forces acting along the three mutually perpendicular directions in the anionic framework. If these forces are equal, the crystals form a stable three-dimensional lattice structure. If the lattice forces are greater in two of the directions than in the third, a layer lattice structure is produced, and if the forces in two of the directions are weaker than that in the third, a "fibrous" or "chain" structure is formed. Zeolites can thus be divided into three classes[11,12]: 1) crystals with a rigid lattice; 2) layer structures; and 3) semi-rigid structures. A characteristic feature of all zeolites is the presence of weakly-held water molecules, which under appropriate conditions may be reversibly removed or replaced by molecules of certain other substances. Unlike water of crystallisation, zeolite water is removed continuously on heating, and not step wise[13]. Zeolites contain interconnected internal channels through which water and certain other "foreign" molecules are able to move.

All zeolites used as molecular sieves (chabazite, faujasite, mordenite, etc.) have a rigid three-dimensional framework formed by rings of SiO_4 and AlO_4 tetrahedra, and this is not distorted on dehydration[14-17]. For example, in the mineral faujasite, which has the highest sorptive capacity, the stable cubic lattice includes large, many-sided holes or "super-cages". The shape of these cages resembles that of a sphere with sections cut off, the perimeter of each "cut" being formed by a ring of many tetrahedra[18].

Fig. 1 illustrates a structure showing the arrangement of hexagonal prisms characteristic of chabazite, and Fig.2 shows the superposition of cubo-octahedra characteristic of faujasite[19].

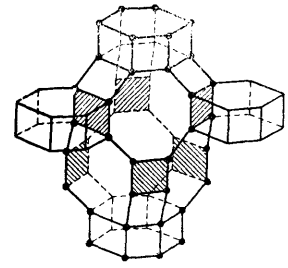


Fig. 1. Arrangement of hexagonal prisms characteristic of chabazite.

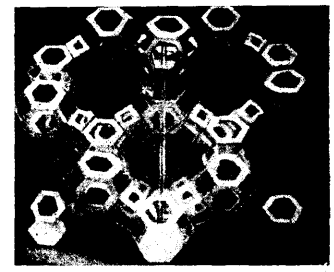


Fig. 2. Superposition of cubo-octahedra, characteristic of faujasite.

TABLE 1. Characteristics of some natural molecular sieves.

Property	Chabazite	Gmelinite	Levynite	Faujasite	Mordenite	Reference
Approximate chemical composition	$(Ca,Na_2)\cdot O\cdot Al_2O_3\ 4SiO_2\cdot 6H_2O$	$(Na_2,Ca)\cdot O\cdot Al_2O_3\ 4SiO_2\cdot 6H_2O$	$CaO\cdot Al_2O_3\ 3SiO_2\cdot 5H_2O$	$(Na_2,Ca)\cdot O\cdot Al_2O_3\ 5SiO_2\cdot 10H_2O$	$(Ca,K_2;\ Na_2)\cdot O\cdot Al_2O_3\cdot 10SiO_2\cdot 6.6H_2O$	22
System	trigonal	pseudotrigonal	trigonal	cubic	monoclinic	22
Crystal form	rhombohedra	hexagonal, sometimes trigonal	rhombohedra	octahedra		8
Specific gravity	2.08—2.16		2.09—2.66	1.92	2.15	8
Hardness	4—5			5	4—5	8
Volume occupied by water, $cm^3\ g^{-1}$	0.214	0.211	0.184	0.281	0.135	22
Sources	Czechoslovakia, Iceland, Australia (near Melbourne)	regions of volcanic activity		very rare, found near Baden	Morden-Kings (USA)	8

TABLE 2. Characteristics of some synthetic molecular sieves.

Adsorbent	Cell dimensions, Å	Free diameter of the largest cage	Type of "window" connecting the largest cage	Free diameter of the "windows", Å	Largest molecules penetrating the dehydrated crystal	Maximum number of molecules accommodated by the largest cage	Free pore volume (cm^3 per cm^3 of crystal)
Chabazite, calcium form	$a=13.78, c=14.97$ (hexagonal)	7.5 by 11.5 (oblong cage)	8-membered rings, 6 per cage	3.9 6 per cage	normal paraffins ($d=4.9$ Å)	12—14 H_2O 6 A; N_2; O_2	0.46
Linde synthetic zeolite 5A	12.27 (cubic)	~11.8	ditto	~4.2; 6 per cage	ditto	~29 H_2O; 12 A; O_2	0.46
Synthetic adsorbent similar to faujasite	24.8 (cubic)	~12	12-membered rings, 4 per cage	9—10 Å 4 per cage	Readily occludes n-, iso-, and neo-paraffins, aromatics, and naphthenes. Largest molecule not determined	32 H_2O 17—19 A, N_2, O_2 ~4.5 n-C_5H_{12} ~2.8, iso C_8H_{18} ~5.4 C_6H_6 ~4.1 cyclohexane	0.53

The group with semi-rigid structures includes the "fibrous" zeolites (the natrolite group) formed by chains of (Si—Al)—O tetrahedra[20]. Dehydration leads to displacement of the atoms around the spaces holding the water, but the chain length is not shortened appreciably. In zeolites of the heulandite group (heulandite, phillipsite, etc.), the planar lattice layers are separated by water molecules and cations which hold the anionic layers together. The dehydration of layer zeolites is accompanied by a considerable decrease in volume in one direction. Sorption in fibrous and layer zeolites is much weaker than in zeolites with a rigid lattice: the former can occlude only polar molecules such as H_2O or NH_3, with an increase in volume.

Table 1 gives data for natural zeolites with molecular-sieve properties. The unit cell of the Linde molecular-sieve lattice is a cubo-octahedron. These are joined in sixfold coordination in the Linde type A adsorbents and in tetrahedral coordination, like the diamond structure, in the type X adsorbents (Table 2)[8,21].

The most open lattice structure is shown by synthetic zeolites analogous to the mineral faujasite (molecular sieve 13 X). Electron microscopy has shown that the powdered material is made up of small cubes[23]. Various derivatives can be prepared from the sodium form of faujasite by cation exchange with salts of potassium, ammonium, methylamines, magnesium, calcium, strontium, barium, etc. (molecular sieve 10 X is the calcium form of faujasite). The sodium form has the composition $Na_2O\cdot Al_2O_3\cdot 2.67SiO_2\cdot mH_2O$, where m depends on the moisture content of the air. According to Barrer and Sutherland's data[24], faujasite crystals (at a relative pressure $P/P_0 = 0.25$) adsorb a volume of sorbate (calculated as the liquid) equal to approximately half the volume of the adsorbent (from 0.54 for nitrogen to 0.41 for isooctane). The number of molecules occluded by one faujasite 24.8 Å cell varies between 254 (for water) and 22 (for isooctane).

The composition of zeolites may vary, even in material from the same deposit, as a result of partial substitution of one cation by another and by changes in the $Al_2O_3:SiO_2$ ratio, which in chabazite, for example, can vary from 1:2.3 to 1:6.[17,25]

In the zeolites used as molecular sieves the relative volume occupied by the cavities in the lattice is very large. Barrer[22,26] gives the following values for this volume, as percentages of the total zeolite volume:

faujasite	56	levynite	40
chabazite	47—50	mordenite	28—33
gmelinite	50		

The considerable inter-lattice volume gives molecular sieves high sorptive capacity. The stable three-dimensional lattice of zeolites of this type enables them to withstand prolonged heating at 300°—450° and reduced pressure without undergoing any significant structural changes. Evacuation in this way is used to remove the water inside the crystals before using the mineral as a sorbent.

Barrer[22] has classified molecular sieves into 4 categories, depending on the minimum cross-sectional area of the channels:

Class A (faujasite) has the largest channel cross-section and readily absorbs normal and iso-paraffins (up to isooctane) and all molecules which can be occluded by the other classes: the free channel diameter is approximately 6 Å* [27].

Class B (chabazite, gmelinite, and the synthetic zeolite $BaO \cdot Al_2O_3 \cdot 4SiO_2 \cdot H_2O$) has a minimum channel diameter of ~4.9 Å, does not adsorb iso-paraffins or aromatic hydrocarbons, adsorbs methane, ethane, and smaller molecules rapidly, and normal paraffins from propane to heptane slowly [29].

Class C (sodium mordenite) [channel dia 4.0 Å (Ed. of Translation)] does not adsorb aliphatic hydrocarbons beyond ethane; methane and ethane are occluded slowly, and N_2, CO, H_2O, and smaller molecules are adsorbed fairly rapidly.

Class D (levynite, potassium mordenite) has a minimum channel diameter of ~3.8 Å, occludes nitrogen and molecules of smaller cross-section; argon, HCl, and NH_3 are adsorbed slowly; hydrocarbons and their derivatives are hardly adsorbed at all.

THE PREPARATION OF SYNTHETIC ZEOLITES

Before considering methods for preparing synthetic molecular sieves, we must examine the origin of natural zeolites. It has been suggested [30] that they have been formed by the prolonged mineralising action of solutions (the so-called hydrothermals) on rocks at high temperatures (100°–350°) and relatively high alkalinity. Chabazite is most frequently found in cavities in basalts, and is deposited in the outflow from some hot springs. Gmelinite occurs in many regions of volcanic activity. Mordenite deposits are generally richer, and large quantities are found in the Morden-Kings basalts (USA).

Most methods for preparing synthetic zeolites imitate the natural geochemical processes, since zeolites and clays can be formed in superheated aqueous solutions under pressure [31-33].

Under laboratory conditions the hydrothermal synthesis of zeolites is carried out in small stainless-steel autoclaves; in some cases a silver vessel is placed inside [31,34-40]. The starting materials are usually a solution of sodium aluminate and an aqueous suspension of silicic acid containing some alkali [41]. This mixture yields an aluminosilicate gel of the required composition. A weighed specimen of gel is placed in the autoclave, water is added, followed in some cases by a slight excess of alkali, the autoclave is hermetically sealed and placed in an air thermostat with heater. After the necessary time interval, the autoclave is cooled, the product is washed with water at ~100° and dried. Before the adsorptive properties are studied, the zeolite is heated at 350° under reduced pressure for several hours.

Many syntheses have been carried out to examine the effect of such factors as temperature, duration of reaction, alkalinity of the medium, quality of the original gel, and occlusion of salts. The crystallisation temperature of the zeolite varies over a wide range from 60° to 450° [31]. The optimum temperature for the formation of mordenite, for example, is 265°–295° [41], and a mineral similar to chabazite has been obtained at 150° [25].

The duration of the reaction can vary over very wide limits: the alkali-metal aluminosilicates crystallise fairly rapidly, sometimes in a few hours, but gels containing calcium or barium cations crystallise slowly, sometimes requiring several weeks [31]. In some cases (for example, the crystallisation of mordenite in a strongly alkaline medium) a good yield of zeolite is obtained in 24 h, and after 2 days recrystallisation is observed, with the formation of a different phase which is more stable under the given conditions.

In a paper on the hydrothermal synthesis of potassium aluminosilicates Barrer and Baynham [42] reported that the time required for crystallisation with high yield increased as the reaction temperature was lowered. At 300° and above not more than 16 h was necessary, but 3–4 days were necessary for some crystallisations below 150°.

It has been assumed that the formation of highly-hydrated materials such as zeolites requires a high water-vapour density, so that increased pressure favours the synthesis. The pressure in the autoclaves has been raised to several hundred atmospheres, but since the temperature was below the critical temperature, water was always present in the liquid state and acted as mineraliser. The crystals often separated very slowly and, once formed, did not grow any further [30].

The success of the hydrothermal crystallisation depends to a great extent on the conditions of preparation of the aluminosilicate gel. In a study of the laboratory synthesis of mordenite Barrer [41] examined the influence of dehydration of the silica gel on the yield of zeolite. Good yields of mordenite were obtained irrespective of the rate of evaporation on a water bath. Drying above 110° makes the aluminosilicate gel insoluble and leads to unsatisfactory crystallisation. Later, Barrer and Baynham [42] omitted the evaporation of the water, since it was found that this preliminary ageing retards the crystallisation at temperatures below 200° (the evaporation was not omitted in the synthesis of mordenite, which crystallises above 200°). The effect of gel drying was not significant, however, when the hydrothermal crystallisation was carried out at high temperature (above 350°) or in strongly alkaline medium [43].

The alkalinity plays a particularly important part in the hydrothermal crystallisation of zeolites, and their crystals grow best at a pH of 8–12. For this reason, Barrer and coworkers maintained the ratio

$$\frac{(R^{II}, R^{I}_2)O}{Al_2O_3} = 1$$

in the synthesis of aluminosilicates. Layer-lattice aluminosilicates of the kaolin or montmorillonite type are formed at lower alkalinity [31]. When the alkalinity is reduced, the crystallisation is retarded, probably due to the insufficient solubility of the gel, and fewer, finer crystals are formed [41]. From a large number of experiments, Barrer concluded that in hydrothermal reactions the pH is as important as temperature and composition. In laboratory experiments the pH has usually been 8–10.5. In the synthesis of mordenite increase in the pH above 10.0 facilitates recrystallisation to analcite [43].

Table 3 gives some of Barrer's experimental data on the preparation of mordenite [41], and Table 4 gives the

* One patent reports that faujasite dehydrated at 250° under reduced pressure can be used to separate molecules with an effective diameter of ~14 Å from molecules with a larger cross-sectional area [28].

TABLE 3. Composition of gel: $Na_2O.Al_2O_3.10.9SiO_2.nH_2O$.

Reaction conditions		pH of cold mother liquor after reaction	Reaction product
temp., °C	duration		
~295	2 days	~10	good yield of mordenite and some analcite
~290	ditto	9.5—10	mordenite, some analcite
~295	»	~9	excellent yield of mordenite
~295	»	~7.5	mordenite, some analcite; poor crystallisation
~280	»	10—10.5	few mordenite crystals, corroded; some analcite
~290	24 h	~10.5	good yield of mordenite and some analcite
~280	17 h	—	good yield of mordenite

TABLE 4. Composition of original gel: $K_2O.Al_2O_3.nSiO_2$.

Temperature, °C	pH	n	Reaction product
150	>10.5	1—2	moderate yield of zeolite of composition $K_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 3H_2O$
150	>10.5	3	moderate yield of above zeolite or chabazite (depending on the alkalinity)
150	>10.5	4—6	good yield of chabazite
85	>10.5	7—8	good yield of phillipsite, $K_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 3H_2O$, and chabazite

experimental conditions used by Barrer and Baynham for the preparation of potassium chabazite[42].

Comparison of the X-ray diffraction patterns of synthetic specimens with those of natural chabazite converted to the potassium form by ion exchange shows that the specimens of highest silica content (approximate composition $K_2O.Al_2O_3.4.15SiO_2.4.4H_2O$) have structures closest to that of natural chabazite.

Molecules of the salts NaCl, KCl, KBr, $BaCl_2$, etc., present in high concentration in the mother liquor, often enter the inner channels of the growing crystals as "fillers", facilitating the formation of a very open aluminosilicate lattice. These "foreign" molecules can sometimes be removed by hydrothermal extraction with water, without breakdown of the lattice[31].

Barrer[30,44,45] used this method to prepare a new material, with molecular-sieve properties, from analcite or aluminosilicate gel, with barium chloride or bromide as mineraliser. Data from the most successful experiments are given in Table 5. The original mineral or gel was ground to a powder, mixed thoroughly with solid barium chloride ($BaCl_2$: mineral volume ratio = $\frac{1}{2}$ to $1\frac{1}{2}$) after which water was added (water : solid volume ratio = $\frac{1}{2}$ to 1). The use of saturated or almost saturated barium salt solutions is recommended. Analogous exchange can be carried out with calcium[46].

After extraction of the excess salts with water, the specimens of the new product were found to be extensively hydrated, with a stable three-dimensional lattice similar to that of mordenite or chabazite[44]. Study of the adsorption by the new mineral of substances with different molecular dimensions confirmed that they belonged to the chabazite class. This zeolite has a particular affinity for polar gases, and ammonia is adsorbed strongly even at 300°.

Molecular sieves can thus be prepared not only by direct synthesis, but also by recrystallisation of certain minerals in concentrated salt solutions.

The American worker Sensel[47] recommends, for the hydrothermal synthesis of a hydrated aluminosilicate corresponding to molecular sieve 4A, the maintenance of a stoichiometric component ratio corresponding to the formula $Na_2O.Al_2O_3.2SiO_2$ (a small excess of alkali is permissible), a temperature in the range 65°–160° (best results at 105°–140°), and a reaction duration of 4–24 h. The weight of water should be 80–90% of the total autoclave charge, and the optimum dehydration temperature is 150°–315°. Three-fold treatment with concentrated $CaCl_2$ solution (5 N) at the boil leads to replacement of up to 80% of the sodium cations by calcium, and the zeolite first obtained is converted to an adsorbent of molecular sieve type 5A.

Similar conditions are used in a method for the preparation of molecular sieves described in McCormick and Westerland's patent[48]. A solution containing silicate, aluminate, and metal ions is heated to 80°–100°, mixed thoroughly, and kept for at least 5 h until the zeolite crystal lattice has formed. This method was used to prepare molecular sieves of composition $(0.9 \pm 0.2)M_{2/n}O.Al_2O_3.(2.5 \pm 0.5)SiO_2.(0-8)H_2O$ and $(1 \pm 0.2)M_{2/n}O.Al_2O_3.(1.85 \pm 0.5)SiO_2.(0-6)H_2O$.

A patent by Milton[49] describes the preparation of an aluminosilicate of the 4A type, with composition $Na_2O.Al_2O_3.1.85SiO_2.5.1H_2O$. An aluminate gel enriched with alumina, obtained from a mixture of $NaAlO_2$, Na_2SiO_3, and NaOH solutions, was heated at ~100° for periods varying from 15 min to 90 h. In the same way a gel with increased silicic acid and sodium oxide content yielded a zeolite of type X, with approximate composition $0.9Na_2O.Al_2O_3.2.5SiO_2.6.1H_2O$, close to that of the mineral faujasite.

TABLE 5. Conditions for the hydrothermal synthesis of barium zeolite[45].

No.	Aluminosilicate component	Hydrothermal treatment conditions	Temp., °C	Yield of mineral
1	natural analcite	5 successive treatments with fresh portions of $BaCl_2$ and H_2O, for 12 h each	270	excellent
2	synthetic analcite $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$	6 treatments with $BaCl_2$ and water for 24 h each	210	excellent
3	aluminosilicate gel $K_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot nH_2O$	heated for 6 days with one portion of H_2O and $BaCl_2$	180	excellent
4	gel $BaO \cdot Al_2O_3 \cdot 4SiO_2 \cdot nH_2O$	heated for 3 days with $BaCl_2$ and H_2O	235	good
5	gel $BaO \cdot Al_2O_3 \cdot 4SiO_2 \cdot nH_2O$	ditto	270	moderate
6	synthetic analcite	two successive treatments with fresh portions of H_2O and $BaBr_2$ for 48 and 30 h	205	excellent
7	gel $BaO \cdot Al_2O_3 \cdot 4SiO_2 \cdot nH_2O$	heated for 1 day with a concentrated $BaCl_2$ solution at 210°, then for 2 days at 197°	210—197	good

Extraction

Product No.	Water : mineral ratio	Number of extractions	Extraction conditions
2	15 : 1	10	24 h each at 210°
7	15 : 1	7	36 h each at 208°

X-Ray powder methods have shown that the structures of synthetic and natural zeolites are closely similar. For example, the spacings and relative intensities of the lines for natural mordenite are close to those for synthetic sodium mordenite and sodium mordenite prepared by ion exchange[41]. Complete agreement in such cases is not to be expected, since chance inclusions and partial replacement of cations are possible in the natural materials.

In 1949 an experimental study of the synthesis of zeolites was begun in the Linde research laboratory, where a large number of specimens were synthesised, including zeolite "X" of composition $M_{86/n}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 267H_2O$ (where n is the valency of the cation), with lattice structure similar to that of faujasite[50]. Workers in the same laboratory also synthesised a few cubic zeolites, with unit-cell composition corresponding to the formula $Na_{12}[(AlO_2)_{12} \cdot (SiO_2)_{12}] \cdot 27H_2O$ and effective pore diameter 4.2 Å [51,52]; the spaces within the crystals after dehydration made up 45% of the volume. Replacement of ~30% of the Na^+ cations by Ca^{2+} increases the effective pore size of the zeolite to 5 Å and the free pore volume accessible to water reaches 48%. The calcium form of type A (sieve 5A) occludes straight-chain hydrocarbons up to and including tetradecane.

Work has also been carried out recently in the USSR on the synthesis of zeolites and the study of their adsorptive properties[53,54].

Barrer and coworkers have given data on the synthesis of a number of zeolites at comparatively low temperatures. Study of sodium aluminosilicate crystallisation fields at comparatively low temperatures[55] led Barrer and Baynham and others to the conclusion that since the zeolites are "filled" structures in which the filler is water, they should be more readily formed at low temperatures (in the absence of high pressures), because of the volatility of the filler. The laboratory experiments on the synthesis of zeolites in the range 60°–110° were carried out in sealed heat-resistant glass tubes; those at higher temperatures were carried out in stainless steel autoclaves, since under these conditions the aluminosilicate gel reacts with glass. The crystallisation often took place very readily and rapidly. A zeolite of the 4A type ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$) was obtained in good yield from a gel enriched with alumina, at 85°–110° after only 2–3 h. The time required for crystallisation increases with increase in the silica content of the gel. The gel crystallises more rapidly in the presence of a large excess of alkali, particularly at 60°–85°.

The Linde company supplies molecular sieves of the 4A (pore diameter ~4 Å), 5A, and 13X types in the form of powder or solid stable granules. The latter are made by mixing the powdered zeolite with a binder, moulding to the required shape, and drying. Binders used include clay, attapulgite[56], gelatinous aluminium hydroxide[57,58], starch, a high-molecular-weight fatty acid, a heavy metal stearate[59] or "sterotex" — a hydrogenated vegetable oil[47], which is burnt off in the dehydration process.

Barrer[19] has published a table giving the specific surfaces of crystals and other sorbents (Table 6).

THE SORPTIVE PROPERTIES OF ZEOLITES

The sorptive properties of zeolites differ sharply from those of other adsorbents[60].

1. They readily adsorb only those molecules which are able to penetrate into the uniform channels of the structure.
2. The adsorption potential is very high as a result of the superposition of the fields of the opposite walls of the narrow channels, so that the zeolite has a high adsorptive capacity at low adsorbate concentrations.
3. For the same reason, zeolites have a high adsorptive capacity at high temperatures.
4. Since zeolites are polar sorbents, they have a high affinity for polar molecules, particularly water molecules, and they also show selective adsorption of unsaturated organic compounds.

Adsorption on zeolites has been studied by many workers[61-66]. The shapes and dimensions of the adsorbate molecule and zeolite channels determine whether or not a given molecule will penetrate into the crystal. The cross-sectional area in the narrowest places should be greater than the corresponding critical dimensions of the sorbate molecules, which for spherical molecules will be equal to the diameter, and for other symmetrical molecules will be the maximum cross-sectional area perpendicular to their length. For an asymmetric molecule, the critical dimension will be the diameter of the circle which encloses the maximum cross-sectional area of the molecule in the plane perpendicular to its length[22]. Differences in the size and shape of molecules are illustrated in Fig. 3.

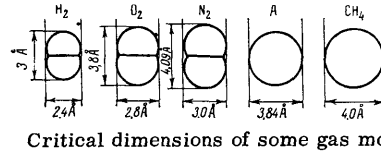


Fig. 3. Critical dimensions of some gas molecules.

TABLE 6. Specific surfaces of some porous materials.

Porous crystal	Specific surface, $m^2 g^{-1}$	Active sorbent	Surface, $m^2 g^{-1}$
Linde sieve 13X	1030	"Carbolac" carbon	1060
Linde sieve 10X	1030	Carbon black powder	770
Linde sieve 4A	~800		
Linde sieve 5A	750–800	Silica gel	610
Calcium chabazite	750		
		Activated alumina	230–380
Mordenite	440	Sepiolite	310 (max)
Methylammonium bentonite	160	Attapulgite	260 (max)
Dimethylammonium bentonite	150		
Trimethylammonium bentonite	130	"Vycor" porous glass	140
Tetramethylammonium bentonite	140		

The molecules of normal hydrocarbons have identical cross-sectional areas and all of them, up to heptane, penetrate into the channels of zeolites of type 5A, but the rate of adsorption decreases with increase in chain length[67-69]. Barrer used the experimental data to construct a table[22] characterising the selectivity of the occlusion of different substances by the three classes of zeolite (Table 7).

Barrer divided all the compound studied into groups[22,70] according to the nature of their sorption by molecular sieves. If the molecules of a given substance are adsorbed by a given sorbent, it would be expected that other molecules in the same group should also be occluded by

TABLE 7. Selectivity of molecular sieves of classes B, C, and D towards various materials.

Class of zeolite	Typical molecules occluded rapidly at room temperature or below	Typical molecules occluded at a moderate rate at room temperature or above	Typical molecules not occluded appreciably at room temperature or above
B	He, Ne, A H_2, N_2, O_2 CO, CO_2, COS, CS_2 H_2O, HCl, HBr NO, NH_3 CH_3OH, CH_3NH_2 CH_3CN, HCN $Cl_2, CH_3Cl, CH_3Br, CH_3F,$ CH_2Cl_2, CH_2F_2 CH_4, C_2H_6, C_2H_5OH HS, CH_3SH	$CH_3CH_2CH_3$ and higher n-paraffins $C_2H_5OH, C_2H_5NH_2$ $C_2H_5F, C_2H_5Cl, C_2H_5I$ I_2, HI C_2H_5SH $HCOOCH_3, HCOOC_2H_5$ C_2H_5CN, CH_3COCH_3 CH_2Br_2 CH_3COOCH_3 $NH(CH_3)_2, NH(C_2H_5)_2$	Aromatic, cyclo-, and iso-paraffinic hydrocarbons and their derivatives Heterocyclic compounds such as thiophene, and pyridine CCl_4, $CHCl_3$, $CHCl{=}CCl_2$, CH_3CHCl_2, $CHCl_2CCl_3$, C_2Cl_6 and analagous bromo- and iodo-compounds Secondary alcohols, mercaptans, nitriles, and halides Primary amines with one NH_2 group at a secondary C atom Secondary and tertiary amines Ethers with branched chains and thioethers
C	He, Ne, A H_2, O_2, N_2 CO, NH_3, H_2O	CH_4, C_2H_6, CH_3Cl CH_3OH, CH_3NH_2 HCN, Cl_2, CH_3F, CH_3CN	All molecules in columns 3 and 4 for zeolites of class B
D	He, Ne, A $H_2, O_2, N_2,$ H_2O	A HCl NH_3	All molecules in column 4 for zeolites of class C, and also CH_4, C_2H_6, CH_3OH, CH_3NH_2, CH_3SH, CH_3CN, CH_3Cl, CH_3F

TABLE 8. Adsorption of linear, branched and cyclic hydrocarbons on molecular sieve 5A, silica gel, and activated carbon.

Adsorbate	Temp., °C	P, mm Hg	Wt.% of substance adsorbed		
			mol. sieve 5A	silica gel	activated carbon
n-Butane	25	47	9.8	3.4	24
Isobutane	25	98	0.5	4.8	26
Benzene	25	50	0.5	9.5	44

Molecular sieves have a high affinity for water vapour. At low moisture concentrations the adsorptive capacity of a molecular sieve is 6–10 times greater than that of silica gel or activated alumina. Fig. 5 gives isotherms for the sorption of water vapour on a molecular sieve, silica gel, and alumina gel[2]. Thus 1 g of zeolite type A adsorbs 20–22% of water at a relative humidity of 10%, and 10% water at a water-vapour pressure of 0.005 mm Hg[51].

that sorbent. If, for example, in the series $CHCl_3$, $(CH_3)_3CH$, $(CH_3)_2{=}CHCl$ and $CHBr_3$, the standard molecule $(CH_3)_3CH$ is not adsorbed by a zeolite of class B, then the other molecules in this series, which are similar in size and shape, will not be occluded.

The selective behaviour of small molecules compared with larger molecules is illustrated quantitatively by the data in Table 8 [71]. Activated charcoal and silica gel adsorb all three substances. The 5A molecular sieve readily adsorbs the straight-chain compound n-butane but hardly adsorbs isobutane or benzene at all.

Milton and Breck's patent[72] on the use of faujasite as adsorbent for molecules whose maximum cross-sectional area is less than that of the $(C_4F_9)_3N$ molecule gives the composition of typical faujasite specimens as 0.43–0.58 Na_2O, 0.41–0.54 CaO, and 4.54–5.00 SiO_2, per g of Al_2O_3. The same patent also gives the data for adsorption by faujasite reproduced in Table 9 (as wt.% of adsorbent).

Thermodynamic aspects of intracrystalline sorption by faujasite have been discussed by Barrer and Stuart[73].

The chief advantage of molecular sieves is their ability to adsorb relatively large quantities of substances present in low concentrations in mixtures. Fig. 4 gives isotherms for the sorption of oxygen, nitrogen, and straight- and branched-chain hydrocarbons by molecular sieves of types 5A and 4A, chabazite, and silica gel[51]. In all cases the isotherms for the zeolites rise sharply at very low concentrations and the quantity of substance adsorbed changes little with further increase in the sorbate concentration.

The high adsorptive capacity at low concentrations makes it possible to use molecular sieves for drying and purifying gases and non-polar liquids, and also for trapping valuable impurities present in small quantities in effluent gases from the chemical and petroleum industries.

TABLE 9. Adsorptive properties of faujasite.

Adsorbate	Temp., °C	Partial press., mm Hg	% of wt. of adsorbent	Adsorbate	Temp., °C	Partial press., mm Hg	% of wt. of adsorbent
Propane	25	10	2.9	p-Xylene	25	0.06	10.6
		168	9.3			6.7	19.7
1-Butene	25	0.45	7.7	Krypton	—183	0.005	11.1
		156	17.0			0.14	50.0
Argon	—196	0.092	20.0	Carbon monoxide	25	43	3.5
		9.0	31.9			708	14.6
Isobutane	25	10	8.7	Water	25	0.007	10.1
		743	12.9			23	33.4
Cyclohexane	25	0.06	10.6	Oxygen	—196	0.033	13.9
		92	17.0			121	29.3
Benzene	25	0.045	7.2	Nitrogen	—196	0.010	13.7
		0.85	23.0			310	23.6
				Neopentane	25	0.3	8.9
						404	14.9

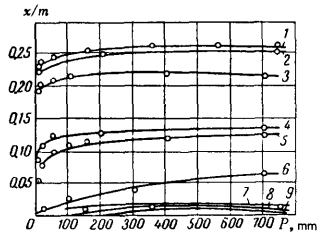


Fig. 4. Isotherms for sorption on a zeolite of type A, chabazite, and silica gel: 1) O_2 on zeolite at -183°; 2) N_2 on calcium zeolite at -196°; 3) N_2 on chabazite at -196°; 4) propene on calcium zeolite at 25°; 5) propane on calcium zeolite at 25°; 6) propane on silica gel at 25°; 7) propane on zeolite A at 25°; 8) N_2 on zeolite at -196°; 9) isobutane on chabazite or calcium zeolite at 25°.

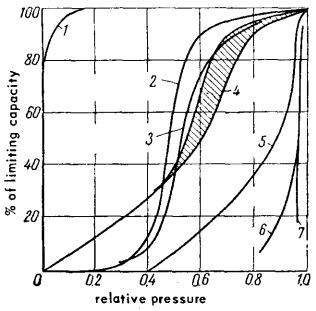


Fig. 5. Sorption of water vapour on different materials, expressed as % of the limiting sorption volume: 1) chabazite; 2) sugar charcoal; 3) pure coke carbon; 4) silica gel; 5) birch charcoal; 6) platinum; 7) glass.

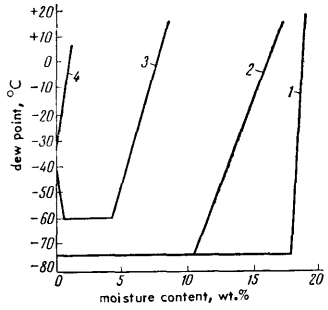


Fig. 6. Dependence of the dew point on the quantity of adsorbed moisture for a molecular sieve (1, 2, and 3) and silica gel (4): 1) at 24°, $V = 19.81$ mm sec^{-1}; 2) at 100°, $V = 19.81$ mm sec^{-1}; 3) at 95°–114°, $V = 19.81$ mm sec^{-1}; 4) at $V = 1.58$ mm sec^{-1}.

Molecular sieves also have a high adsorptive capacity under dynamic conditions. Fig. 6 shows the dependence of the dew point on the quantity of adsorbed moisture, before break-through, on a molecular sieve and on silica gel at a 6–10% relative humidity of the incoming air and a column length of 75 cm.[71] The lowest dew point is given by the molecular sieve. Break-through is observed when 17–18% of water has been adsorbed by the zeolite, whereas the figure for silica gel and alumina gel is much smaller. A molecular sieve can thus be used to dry gases more efficiently. It is possible to use smaller absorbers to achieve the same efficiency, and regeneration of the sorbent requires less heat than the removal of the moisture adsorbed by silica gel or alumina gel.

Since the zeolites hold the adsorbed molecules firmly, they retain their adsorptive power at low and high temperatures. Fig. 7 shows isotherms for the sorption of water vapour on a molecular sieve of type A, silica gel, and alumina gel at different temperatures[60]. Isotherms for sorption at different temperatures on silica gel, alumina gel, etc. have been compared by Breck et al.[51]

Zeolites adsorb water intensively at 75°–100°, while silica gel and alumina gel lose their adsorptive power at these temperatures.

Another distinctive feature of molecular sieves is their high affinity for polar molecules, which is apparently due to the electrostatic nature of the adsorptive forces[74]. This is illustrated by the isotherms for the sorption of the polar gas carbon monoxide and the non-polar gas argon (Fig. 8)[71]. Although these two substances are equally volatile and have sufficiently small critical molecular diameters to be adsorbed by a 5A molecular sieve, the sorption isotherm for carbon monoxide lies considerably higher than that for argon.

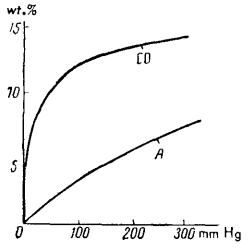


Fig. 8. Isotherms for the sorption of CO and A on molecular sieve 5A.

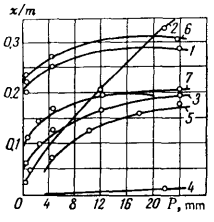


Fig. 7. Isotherms for sorption of water vapour on a molecular sieve of type A, silica gel, and alumina gel at different temperatures: 1) zeolite A, 25°; 2) silica gel, 25°; 3) zeolite A, 100°; 4) silica gel, 100°; 5) alumina gel, 25°; 6) calcium zeolite, 25°; 7) calcium zeolite, 100°.

Molecular sieves also show a marked affinity for unsaturated molecules. For example, at a pressure of 1 mm Hg a molecular sieve adsorbs 3.8% C_2H_2 and only 0.3% C_2H_6.[75] This property of molecular sieves is widely used in industry to separate acetylene, ethylene, butylene, etc. from saturated molecules of approximately the same size[60]. The separation coefficient for an ethane–ethylene mixture is 1.5 on activated charcoal, 3.0 on silica gel, and 20 on a molecular sieve[75].

The thermodynamic and energetic aspects of adsorption on zeolites have been examined by several workers[12,68,76–80].

THE SEPARATION OF MIXTURES BY MOLECULAR SIEVES

The successful separation of gas mixtures on molecular sieves depends on two main factors: (1) the difference in the rates of occlusion of the gases, which depends on the differences in the shape and size of the molecules, and (2) the relative affinity of the crystal for the substances being sorbed.

The separation is particularly efficient if the rapidly--diffusing molecule also has a high affinity for the adsorbent. If, however, the molecules with high affinity for the sorbent diffuse slowly, they may interfere with the adsorption of other molecules, and lead to "poisoning of the sorbent", making it unsuitable for the separation of the mixture [22,81].

Molecules can be "sifted out" of mixtures by zeolites either by a static method in which the immobile liquid or gas comes into contact with the vacuum-dehydrated adsorbent or by a flow method in which the mixture passes through a layer or column of the zeolite. By selecting a suitable flow rate, it is possible to separate completely the component which is adsorbed rapidly, from the component which is occluded slowly.

The adsorption is usually carried out in such a way that approximately half of the internal pore volume is saturated; the sieve is then regenerated by heating at 300°–350° under reduced pressure for several hours. In cases of slow desorption, for example in the removal of occluded long--chain hydrocarbons, the sorbate is partially extracted with superheated water [26].

The temperature chosen for the separation depends on the composition of the mixture. Since increase in temperature accelerates the adsorption of hydrocarbons, the separation of normal paraffins from iso-paraffins and aromatic hydrocarbons on chabazite has been carried out at an adsorbent temperature of 150°–220° [26]. An ethane–propane mixture is separated at room temperature, and argon is separated from nitrogen and oxygen on mordenite at -183°.

Mordenite has been used to separate the following gas mixtures: nitrogen–argon, hydrogen–nitrogen, neon–argon, and hydrogen–argon [22,82]; quantitative separation of argon from oxygen has been achieved by passing the mixture once over a small quantity of the mineral.

Barrer and Riley have compared the efficiency of activated charcoal, chabazite, and a synthetic zeolite prepared from barium salts, for the separation of the inert gases [44]. At -194.7° and an equilibrium pressure of 10 cm Hg, 1 g of the synthetic zeolite occluded (under standard conditions) 17.5 ml of neon and 0.5 ml of helium, which corresponds to a separation factor of 35; under the same conditions chabazite gave a separation factor of 12 and activated carbon a factor of only 5. Nitrogen is adsorbed much more rapidly than methane from their mixtures on to a Linde 4A molecular sieve and a separation factor of 10 has been obtained [83].

Barrer has patented methods for separating hydrocarbons with molecular sieves (1942) [84,85] and for preparing synthetic zeolites (1946) [45].

Zeolites of type A and chabazite have been used successfully to separate low-molecular-weight n-paraffins from iso--paraffins, and aromatic compounds from naphthenes (Table 10) [22]. Table 11 gives further data on the separation of various mixtures by chabazite.

Monosubstituted derivatives of methane with small substituents, for example OH, CH, CN, Cl, and Br, are occluded rapidly, but the analogous ethane derivatives are occluded slowly. Quantitative separation of these homologues (with the same substituent) can be carried out with an ordinary adsorption column filled with a molecular sieve. Molecular sieves can also be used to separate azeotropic mixtures [22,86] such as $C_2H_5OH-H_2O$, $CH_3OH-(CH_3)_2CO$, H_2O–dioxan, C_2H_5OH–iso-C_7H_{16} (Table 11), and also mixtures whose components have the same b.p., for example, n-heptane–isooctane (Tables 10 and 11).

Mixtures of certain aromatic hydrocarbons have been separated in the laboratory with molecular sieves 10X and 13X [72,87]. A very clean separation of a mixture of hydrogen, oxygen, nitrogen, methane, and carbon monoxide has been achieved on a chromatographic column of Linde 5A

TABLE 10. Separation of mixtures using chabazite (crystalline sieve type B).

Mixture	Components removed	Temperature of adsorbent, °C	Method and conditions
Ethane–propane	ethane	20	flow
Propane–isobutane	propane	150–160	static
Propane–isopentane	propane	150	"
n-Butane–isobutane	n-butane	185, 160	»
n-Butane–isopentane	n-butane	210, 160	»
Propane–n-butane–isopentane	n-butane, pentane	150	»
n-Butane–toluene–cyclohexane	n-butane	216	»
Isobutane–n-pentane	n-pentane	220	»
n-Heptane–isooctane	n-heptane	200	in liquid phase
n-Heptane–toluene	n-heptane	200	ditto
n-Butane–benzene	benzene	160	
Ethane–isobutane	ethane	20	
Ammonia–isobutane	ammonia	160	

TABLE 11. Separation of mixtures using a mineral of class B chabazite.

Mixture	Components removed	Conditions and remarks
$H_2O-C(CH_3)_2OH$	H_2O	liquid, at 20°; rapid and quantitative separation
$H_2O-CO(CH_3)_2$	H_2O	ditto
$H_2O-CH_3CO\ C_2H_5$	H_2O	»
H_2O–dioxan	H_2O	»
$CH_3OH-CO(CH_3)_2$	CH_3OH	»
$CH_3OH-C_2H_5Br$	CH_3OH	»
$CH_3OH-CS_2-CH_3CN-C_6H_6$	CH_3OH, CS_2 CH_3CN	»
$CH_3OH-H_2O-CH_3COOCH_3$	CH_3OH, H_2O	»
$CH_3OH-(COOCH_3)_2$	CH_3OH	sorption of vapour in equilibrium with liquid, complete separation
$C_2H_5OH-C_6H_5CH_3$	C_2H_5OH	liquid, at 20°; slow but complete separation
$C_2H_5OH-(CH_3)_2CHOH$	C_2H_5OH	ditto
$C_2H_5OH-n-C_7H_{16}$	C_2H_5OH	»
$C_2H_5OH-H_2O-(C_2H_5)_2O$	C_2H_5OH, H_2O	»
$C_2H_5OH-CH_3COC_6H_5$	C_2H_5OH	liquid, at 112°; rapid and quantitative separation
$CH_2O-H_2O-CH(CH_3)_2OH$	CH_2O, H_2O	liquid, at 20°; rapid and quantitative separation
$CO_2-CH(CH_3)_2OH$	CO_2	ditto, CO_2 in solution
$H_2S-C_6H_6$	H_2S	ditto, H_2S in solution
$C_2H_5SH-C_6H_6$	C_2H_5SH	liquid, at 50°; partial separation after one week
$NH_2CH_3-C_2H_5OH-N(CH_3)_3$	NH_2CH_3, C_2H_5OH	liquid, at 20°; complete removal of the two components after 16 h.
$NH_2C_2H_5-NH(C_2H_5)_2$	$NH_2-C_2H_5$	ditto; slow but complete separation
$Cl_2-C_6H_6$	Cl_2	liquid, at 20°, Cl_2 in solution; rapid and complete separation

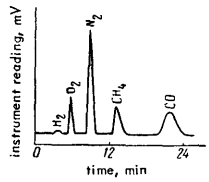


Fig. 9. Chromatogram of the separation of a gas mixture by molecular sieve 5A.

molecular sieve (Fig. 9)[88]. Normal paraffins in petroleum distillates have been separated on a 5A zeolite[89-93]. A method for separating normal paraffins from petroleum by means of molecular sieves (type 5A in particular) has been patented[94,95]. A study has been made of the selective adsorption of boron hydrides (B_2H_6, B_5H_9, $B_{10}H_{14}$) on chabazite, mordenite, and Linde synthetic zeolites 4A, 5A, and 13X[96], and of the adsorption of fluoro-substituted methanes by 4A and 5A sieves[97,98].

The adsorptive efficiency of molecular sieves is directly related to the efficiency of regeneration of the adsorbent. Water in zeolite pores may be removed by heating, and other adsorbed substances present after the zeolites have been used as adsorbents can be removed similarly. If these substances are less strongly held than water, regeneration is possible at lower temperatures. In the case of repeated regeneration, it is recommended that the heating temperatures do not exceed 300°.

Regeneration can be carried out either by heating externally or by passing a hot dry gas through the adsorbent layer. The purifying gas should not form an explosive mixture with the desorption products. After regeneration, the adsorbent is cooled in a current of a dry gas which is weakly held by the zeolite. The adsorbent can also be regenerated by heating at reduced pressure instead of using a stream of gas.

METHODS OF ALTERING THE SELECTIVITY OF ZEOLITES

Both the rate of occlusion of different molecules, and the sorptive capacity of molecular sieves, can be altered in a variety of ways. A definite quantity of a readily-adsorbed substance (usually small polar molecules such as water, ammonia, or methylamine) can be introduced into the crystal[22,99,100]. These modifying molecules enter the channels through which the molecules to be adsorbed must diffuse, and the movement of the latter is restricted. The adsorption is carried out at low temperatures to make the modifying molecules immobile.

For example, the critical size of the oxygen molecule is 2.8 Å, and that of the argon molecule 3.8 Å; under ordinary conditions both are intensively adsorbed by a class C sieve of the mordenite type. When a very small quantity of water (0.05 wt.%) is added to the degassed mordenite, its adsorptive activity towards argon is halved, but the occlusion of oxygen is little affected, so that separation of the mixture is greatly improved. Thus the modifying action of polar molecules involves a decrease in the rate of adsorption of all non-polar gases, but, other conditions being the same, large molecules are retarded to a greater extent than smaller molecules. The modifying molecules create, as it were, a semipermeable membrane between the gas phase and the inner region of the crystal. Optimum conditions for the separation of a mixture are achieved by addition of an appropriate quantity of modifying agent.

A second method of altering the selectivity of molecular sieves is by ion exchange. Since the cations which neutralise the ionic charge of the lattice lie in the channels through which the sorbate molecules move, the rate of occlusion should depend on the size and charge of these cations. Ions of different radii

	Li^+	Na^+	K^+	NH_4^+	Rb^+	Cs^+	Ca^{2+}	Ba^{2+}
r (Å)	0.78	0.98	1.33	1.43	1.49	1.69	1.06	1.33

can reduce the cross-sectional area of the channels to different extents. Additional factors include the mobility of the cations, their tendency to undergo deformation, their charge, their number, and the proportion of hydrate water that they retain on evacuation[101].

In a study of chabazites Rabinowitch and Wood[102] showed that crystals rich in potassium occlude gases weakly, whereas sodium chabazites have greater sorptive power and calcium-rich chabazites adsorb even such large molecules as n-heptane.

Barrer and Baynham[25] prepared an isomorphous series of chabazites of gradually varying composition, from the pure sodium compound to the pure calcium compound, by hydrothermal treatment of natural chabazite with concentrated Ca and Na salt solutions. As the sodium ion was replaced by calcium, the adsorptive power of the chabazite increased sharply, and when the calcium content fell below 35% of the total cation content, the sorptive power decreased sharply, particularly for large molecules.

The experiments showed that a variety of sorbents can be produced from chabazite by the ion exchange $2Na \rightleftharpoons Ca$, combined with other modification processes. Treatment of natural mordenite with concentrated $Ba(NO_3)_2$ and $Ca(NO_3)_2$ solutions, which leads to exchange of the cations and a slight lattice contraction, also changes the sorptive properties of the mineral considerably[76]. X-Ray diffraction patterns show no breakdown of the crystal structure after ion exchange[103]. The thermal stability of minerals modified by ion exchange increases with increase in cation size[104].

It is possible to influence the sorptive behaviour of zeolites towards gases by changing the cation density. The isomorphous replacement of silicon by aluminium increases the anionic charge of the lattice and hence the number of cations per unit cell. The number of divalent cations required to neutralise the anionic charge of the lattice is half the number of univalent cations required, and the cation density of chabazites enriched with Ca^{2+} or Ba^{2+} is accordingly reduced by half. In addition, the ability to retain water between the crystals increases with increase in the polarising power of the cations in the order $K < Na < Ca$; the sorptive capacity of the zeolite is greater the more water it can hold.

The sorptive capacity of chabazites increases with increase in the relative silica content $SiO_2 : Al_2O_3$. The actual process by which the adsorbents are prepared has a modifying effect on their properties. Products of different

sorptive capacity are sometimes obtained from the same starting material under the same conditions. In the hydrothermal synthesis not all the crystals separate immediately and the $SiO_2 : Al_2O_3$ ratio in the first-formed crystals may differ slightly from that in crystals formed later. Some of the crystals may thus have a higher Na^+ ion density and lower adsorptive capacity. Moreover, in hydrothermal treatment with concentrated salt solutions the zeolites may have a tendency to occlude these salts, with deterioration in the adsorptive properties[105]; repeated extraction with hot water is used to remove the salts[19].

The zeolite lattice is more stable the higher the $SiO_2 : Al_2O_3$ ratio. Since the Al–O bond is longer than the Si–O bond, zeolites of higher alumina content should have a lower structural stability[106], and hydrothermal extraction of alumina-rich specimens with prolonged evacuation at 350° does in fact lead to partial breakdown of the crystals[25].

Increase in the number of Al^{3+} ions in the lattice also leads to an increase in the heat of dehydration of the zeolite, owing to the greater anionic charge density[107]. During hydrothermal extraction alumina-rich zeolites lose alkali, undergoing partial hydrolysis, so that some amorphous material is formed. Thus the sorptive capacity of zeolites is influenced by the rate of crystallisation, occlusion of salts, partial breakdown during washing and evacuation, and by isomorphous replacement.

One method of modifying crystalline sieves is to replace the cations by hydrogen. Direct treatment of zeolites with acid leads to decomposition, but if the dehydrated zeolite is heated for a prolonged period in ammonium chloride vapour, the ammonium zeolite is formed[22,108], and when this is heated with oxygen, an intercrystalline reaction takes place between the ammonium cations and the oxygen to form the H-zeolite:

$$4(-O^- \ldots NH_4^+) + 3O_2 = 4(-OH) + 6H_2O + 2N_2.$$

This reaction is possible only if the zeolites can occlude oxygen. Another method for preparing the hydrogen form of zeolites[109] is to replace the cation by Ag^+, which is then replaced by hydrogen by treating the mineral with aqueous pyridine hydrochloride solution.

X-Ray diffraction patterns of the hydrogen derivatives of chabazite and mordenite show the characteristic lattice of the original materials, but the channels are more open than in the usual cationic forms. For example, H-chabazite very rapidly occludes propane, which is adsorbed slowly by the ordinary zeolite: H-mordenite also adsorbs propane, albeit very slowly, whereas ordinary mordenite does not occlude propane at all.

The difference in the rates of sorption of gases is greater at low temperatures, since the effect of the difference in the rates of diffusion increases as the temperature is reduced[22,110]. The influence of temperature on the heats of adsorption of the components of the mixture, that is on the affinity constants, must also be taken into account. If one type of molecule has a higher heat of sorption and a higher diffusion coefficient than the other, decrease in temperature will facilitate separation. If one type of molecule has a higher affinity for the adsorbent but a lower diffusion rate than the other, decrease in temperature leads to less satisfactory separation, since the molecules with the high affinity for the crystal are adsorbed on its surface and diffuse inwards very slowly, preventing the entry of the other molecules.

POSSIBLE TECHNICAL APPLICATIONS OF MOLECULAR SIEVES

As a result of their high adsorptive capacity at low concentrations and high temperatures, and their high affinity for water, unsaturated organic compounds, and other polar molecules, molecular sieves are used, or may find application, in various branches of technology[71]: (1) for drying gases and liquids; (2) for purifying gases and liquids; (3) for removing unsaturated molecules from waste gases; (4) for separating hydrocarbons; (5) as ion exchangers; (6) for maintaining high vacua; (7) as carriers for vulcanising agents for rubber and plastics; (8) for adsorbing isotopes from aerosols; (9) for removing gas samples from low pressure systems, etc. Let us examine their potential applications in more detail.

Molecular sieves as drying agents give more complete removal of moisture than any other adsorbent, and many technical and laboratory applications are possible. They have been used to dry toluene, benzene, pyridine, cyclohexane, acetone, diethyl and dimethyl ethers, ethanol, methanol, transformer oil, etc., most of which can be dried to a moisture content of 0.001%.

One experimental industrial assembly for drying air to very low moisture contents at high pressure by means of zeolites has worked continuously for 18 months[111]. Molecular sieves 4A and 5A have proved 8 times more efficient for drying an inert gas than successive drying with magnesium perchlorate and phosphorus pentoxide[65]. Molecular sieves are used to dry the coolants in refrigerators and thus to prevent corrosion. The oil and the refrigerants (fluorocarbons) have large molecules and are not adsorbed by the sieves[62].

Zeolites may find many applications as highly-active drying agents: (a) as components of packing materials to prevent corrosion of machinery in storage or during transportation; (b) in systems where space is limited and other drying agents cannot be used; (c) in systems operating at high temperatures, etc.

Many industrial gases contain, in addition to water, other undesirable impurities such as CO_2, CO, H_2S, etc., which are readily adsorbed by molecular sieves. These impurities can be removed with the water, thus eliminating the need for several adsorption assemblies[60]. The use of molecular sieves also avoids the corrosion which arises when alkali or monoethanolamine are used to remove CO_2 and H_2S.

One petroleum-chemical company in the USA has devised a scheme for removing CO_2 from ethylene used for polyethylene manufacture, by a single-stage adsorption in an immobile layer of granulated molecular sieve 5A[63]. This system requires a lower capital expenditure than alkali washing, gives efficient CO_2 removal, with simultaneous reduction of the dew point to between -60° and -75°, and does not cause corrosion of the apparatus. The adsorbent is regenerated by the passage of hot methane.

The molecular sieve 5A has been used to remove sulphur compounds and water from liquid propane and for drying transformer oils. Considerable success has been achieved in purifying benzene and toluene from traces of normal paraffins with molecular dimensions less than 5 Å. It has been shown, on the pilot plant scale, that benzene can be purified equally readily in the liquid or gaseous phase, but toluene and xylene are more effectively purified in the gaseous state[71].

The extraction of unsaturated organic compounds from the waste gases of the petroleum-chemical industry by molecular sieves should find extensive application. These compounds are not extracted at present because of the high cost of existing processes. Many gases contain considerable quantities of unsaturated hydrocarbons such as ethylene, propene, and acetylene, which can be used for the synthesis of plastics. Molecular sieves with high selectivity towards these compounds may make their extraction economical.

The use of molecular sieves in the oil-refining and gas industries to separate hydrocarbons also appears promising[67].

High vacua can be obtained by placing molecular sieves in evacuated vessels to adsorb traces of residual gases and moisture[71].

The use of molecular sieves to remove gas samples from systems at low pressure has been suggested[66]. The gas is adsorbed by a zeolite cooled in liquid air, the zeolite is sealed into an ampoule, connected to the analysing apparatus, the ampoule is broken and the gas is desorbed by heating.

The successful use of molecular sieves to adsorb I^{131} from aerosols has been reported[112,113].

Thanks to their uniform structure, molecular sieves have a greater ion-exchange capacity than most commercial resins. As with many organic resins, the sodium from the zeolites can replace cations in solution, e.g. Ag^+, Cu^{2+}, Al^{3+}, Zn^{2+}, Sr^{2+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Au^{3+}, and K^+.

The molecular sieve 4A can separate zinc from cadmium, cobalt from nickel, lithium from sodium, silver from gold, etc. The pH in these exchange reactions should be in the range 5–11.[60,71] Some cations may produce breakdown of synthetic zeolites, for example, barium, copper, and hydrogen.

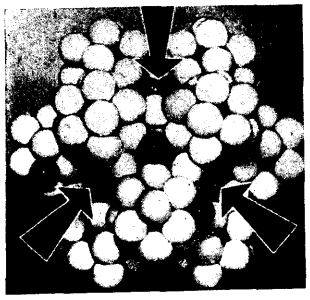


Fig. 10. Model of a molecular-sieve crystal unit[115]. Black spheres represent adsorbed molecules.

The important advantages which molecular sieves have over other ion exchangers are their high exchange capacity and the absence of swelling when wetted.

Molecular sieves have recently found a new use as carriers for certain reagents, particularly vulcanising agents for rubber and plastics, in cases where the reagents could not previously be used because of their volatility, toxicity, or instability. The pores of the zeolites are filled with the reagent, the zeolite is placed in the reaction medium, and the temperature is raised to give gradual liberation of the sorbed molecules, which then react[64,114] (see the model of a unit of a molecular-sieve crystal illustrated in Fig. 10).

The Linde company now supplies several types of chemically "loaded" molecular sieves[115,116,117], which can be used as latent vulcanising agents.

The above examples probably do not represent all the possible applications of molecular sieves, and adsorbents of this type are of interest in several industrial fields.

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DUAL-TEMPERATURE METHODS FOR PREPARING HEAVY WATER

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INTRODUCTION

In the 30 years since the discovery of the heavy isotope of hydrogen, deuterium, in 1931, the production of its compound with oxygen, heavy water, has grown from the preparative scale to several hundred tons per year, as a result of the development of atomic energy programmes.

Heavy water is the best neutron moderator, and its use makes it possible to work with uranium of natural isotopic composition and to decrease considerably the size of the reactor. In a number of cases the heavy water can be used simultaneously as a heat-exchange medium[1] 100–200 tons of heavy water are required for a large-scale reactor.

When estimating the demand for heavy water, it is necessary to consider not only the present demand, which arises from the use of heavy water as moderator and heat-exchange medium in nuclear reactors employing uranium as fuel, but also future requirements resulting from progress in the field of controlled thermonuclear reactions employing deuterium as fuel.

The demand for heavy water for atomic reactors in different countries depends to a great extent on the general trend of the development of the atomic energy programmes. Thus in England, with a high level of atomic energy development, heavy-water reactors are built chiefly for research purposes, so that the demand for D_2O is estimated at 100 tons per year[2,3]. Extensive plans for the construction of heavy-water reactors in Sweden have resulted in an estimated demand of 80 tons per year by 1964 increasing to 400 tons per year by 1974.[4] The demand in Western Germany has been estimated at 100 tons of D_2O per year[5]. The total demand in the Western European countries in the Organisation for European Economic Cooperation will amount to 400–500 tons of D_2O per year by 1965 and 2000–4000 tons per year by 1970.[6-8] The demand in the USA has been estimated at 1000 tons of heavy water per year[9].

The growth of the demand for heavy water for reactors depends to a great extent on the cost of D_2O. According to Harteck's calculations, the use of heavy water becomes economic at a price of 88 dollars per kg of D_2O, and at a price of 22 dollars per kg the cost of the heavy water is insignificant compared with the total cost of the reactor[9]. In the case of a recently-constructed Canadian heavy-water reactor the total cost of 55.8 million dollars included 11 million dollars for heavy water, that is, 20% of the total[10].

Progress in the field of controlled thermonuclear synthesis gives grounds for the expectation that in the near future deuterium will be used as a fuel for thermonuclear reactors. The production of heavy water will then be determined entirely by the energy requirements of a particular country, and the division of countries into rich and poor with reference to sources of energy will disappear, since the raw material, water, is almost equally available in all countries. The cost of the heavy water will not then be important, since the cost per unit of energy will be much smaller than that for coal or oil. According to Kurchatov's calculations, the calorific value of 1000 million tons of coal or oil (the estimated level of production in the USSR by 1975) is equivalent to that of 2000 tons of heavy water used in thermonuclear reactors[11]. The earth's hydrosphere contains 2×10^{14} tons of heavy water, that is the reserves are almost inexhaustible. The development of thermonuclear energy programmes will make heavy water one of the basic materials of atomic technology, instead of an auxiliary material, as it is at present.

We can thus expect, in the near future, a further growth in the production of heavy water, both to satisfy existing demands for it as a moderator in heavy-water energy reactors, and also to meet future demands for heavy water as a fuel for thermonuclear synthesis.

METHODS FOR THE PREPARATION OF HEAVY WATER

Methods of preparing heavy water have been described in a number of review articles[12-32] and in a monograph edited by Murphy[33]. The chief difficulty in the isolation of heavy water is the necessity to deal with vast quantities of raw material, exceeding the quantity of final product by a factor of several tens of thousands, because the concentration of deuterium in natural water is only 0.016 mole %. Since the difference between the properties of deuterium and protium are small, the separation factors of the various methods are small, and the production of heavy water requires a multi-stage counter current process of concentration, carried out in a cascade of multi-stage assemblies.

In principle, all the existing methods of separating isotopes can be used for concentrating heavy water. A number of these are of no industrial importance, however, because of low efficiency (diffusion, thermal diffusion, and adsorption), low separation factors (absorption and extraction), or difficulty in setting up counter current conditions (fractional crystallisation and zone melting), and only the following methods are used industrially: electrolysis of water, electrolysis of water combined with isotopic exchange between water and hydrogen, fractional distillation of water, low-temperature fractional distillation of hydrogen, and dual-temperature exchange between water and hydrogen sulphide. The first three methods were the first to be used to prepare heavy water, but in the last 10 years the last two have become more important[34].

These principal methods for preparing heavy water are normally used in combination, depending on the specific conditions employed. This makes it possible to choose the most convenient combination to give a pure product. The economics of the process are essentially determined by the initial stage of the concentration, which requires the handling of vast quantities of raw material. Calculations show that concentration to 1–2% D_2O accounts for 90% of the total cost of the complete process. The chief factors to be taken into account when selecting the most convenient method of separation are the cost per unit of the product and the possibility of organising its production on a large scale. The processes for preparing D_2O can be classified as independent or dependent on other production processes. The first group includes methods involving distillation of water and the dual-temperature exchange between water and hydrogen sulphide, since the source of deuterium is ordinary water. The second group includes all other methods, whose output is limited by the level of production of hydrogen for the synthesis of ammonia. Some data on the specific capital investment, operating cost, quantities of energy and material used, and separation factors for different methods of preparing heavy water are given in Table 1, which shows that the only methods worthy of serious consideration as far as the cost of the product is concerned are those involving dual-temperature exchange or the low-temperature fractional distillation of hydrogen. This last method, however, is limited by the supply of hydrogen, and cannot satisfy the expected demand for heavy water. According to Weiss, the world production of hydrogen (excluding the USSR) is equivalent to 2800 tons of heavy water per year, assuming 100% extraction[35]. Since all sources of hydrogen cannot be used for the economic production of deuterium and the extraction will always be less than 100%, this figure can be at least halved. Thus distillation of hydrogen can in principle yield considerable quantities of heavy water, but the applicability of the method is limited. The distillation of water has been found to be uneconomic, even under the most favourable conditions, at Wairaki (New Zealand)[37]. Fractional distillation of water and electrolysis are now widely used for the final concentration of heavy water.

The two most economic methods for the production of heavy water on the industrial scale – dual-temperature exchange and low-temperature fractional distillation – were first carried out in the USSR[11,43]. Slightly later, dual-temperature exchange was used in the USA[40], and low-temperature fractional distillation was used in France[44,45] and Western Germany[46,47]. Plants in operation and the chief projects for heavy-water production are listed in another review by the present authors[30]; the volume of heavy-water production in various countries has been reported in a number of publications[34,48,49].

MAIN FEATURES OF THE DUAL-TEMPERATURE METHOD

In a multi-stage counter current process for concentrating isotopes, it is necessary at each stage to transfer the material to be concentrated from one stream to another, that is, to transfer the isotope in which we are interested to another phase which can set up a counter current to the main current of raw material or intermediate product containing the isotope. A large proportion of the total energy necessary for the separation is used up in the "stream transfer". In some cases, the transfer is achieved by evaporation (fractional distillation), and in others by electrochemical or chemical decomposition (electrolysis or chemical methods of isotopic exchange). Harteck and Suess[50] have proposed a method for stream transfer which is based on the use of the temperature dependence of the equilibrium constant for isotopic exchange and involves the addition to the assembly of a supplementary column working at a temperature different from that of the main one. This method has been called the dual-temperature method. All other methods of carrying out isotopic exchange may be termed single-temperature methods. The dual-temperature method was first used for the extraction of deuterium, and it may be carried out in two ways.

1. A cascade of separate pairs of one-stage assemblies is set up, one of which operates at low temperatures and the other at high temperatures (Fig.1). This was the method first suggested by Harteck and Suess[12,50]. Although the dimensions of the stages in the cascade are inversely proportional to the concentrations, this version of the dual-temperature process involves the repeated heating and cooling of the streams and requires large amounts of energy.

2. Two multi-stage columns are connected, one working at low temperature (cold column) and the other at high temperature (hot column). This version of the dual-temperature method was proposed by Geib[12], and Spevack[51], and

TABLE 1. Comparison of different methods of preparing heavy water.

Method	Calculated data				Technical data				Reference
	separation factor	% extraction of deuterium	moles of water treated per mole of product	power required per kg	location of plant	capital expenditure, dollars per kg per year	operating costs, dollars per kg	cost or selling price, dollars per kg	
Electrolysis of water, combined with chemical exchange	7;2.8	60	20 000	70 000 kWh	Trail (Canada) Rjukan (Norway)	500	60	132* 182*	15,24,36 37
Distillation of water	1.04	4	200 000	180 tons of steam at 1,5 atm	Morgantown, Childersburg, Newport (USA) Wairaki (New Zealand)	1100**		390 110—120	15,24,36 37
Distillation of hydrogen	1.4	90	35 000	5000 kWh	Etter (USA), Frankfurt-am-Main project (Western Germany)	375 400	35	73* 80	15,24 38,39
Dual-temperature exchange water–hydrogen water–hydrogen sulphide	 1.22 1.12	 30 18	 40 000 20 000	5000 kWh 8 tons of steam	Savannah River project (USA)	362	30	62	40–42

* Including profit.

** According to Benedict's calculations this figure can be halved [24].

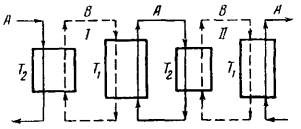


Fig. 1. Dual-temperature process in a cascade of one-stage assemblies. I) First pair of single-stage high-and low-temperature assemblies; II) second pair of single-stage high-and low-temperature assemblies.

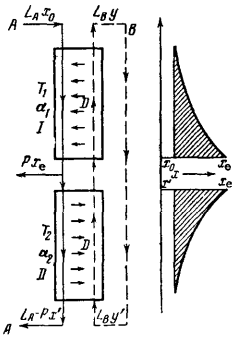


Fig. 2. Dual-temperature process in a cascade of multi-stage columns. I) Cold column; II) hot column.

is illustrated in Fig.2. Column I is the cold column with temperature T_1, at which the separation coefficient is α_1, and column II is the hot column with temperature T_2, at which the separation coefficient is α_2. L_A mole h^{-1} of substance A (for example, water), with deuterium concentration x_0, enters column I. L_B mole h^{-1} of substance B (for example, hydrogen sulphide) circulates through the closed cycle. Isotopic exchange takes place between A and B leading to an increase in the concentration of deuterium in A, the cold column operating as a normal counter current enrichment column in which the deuterium is concentrated in the lower section, in the stream of substance A. This enrichment can in principle be increased to any desired value by increasing the height of column I, if the deuterium concentration of the current B entering the lower part of column I is equal to the deuterium concentration in current A in this part of the column. These concentrations are made equal in the dual-temperature method by means of the counter current stripping column II, through which currents A and B pass in opposite directions at as high a temperature as possible. Deuterium moves from current B to current A in the cold column I, and it moves from current A to current B in the hot column II. Current B extracts deuterium completely from current A in column II only if the separation coefficient is equal to 1 or if the stripping column is infinitely high: in this case the enrichment column I gives complete transfer. Since this extreme case is not attained in practice, the dual-temperature method gives a lower degree of enrichment than a column giving complete transfer between the phases, but the high consumption of energy required for complete transfer is no longer necessary. A much smaller quantity of energy is required to heat currents A and B to the temperature of the hot column and cool them to the temperature of the cold column. This energy can be reduced to a minimum by recovering the heat from the counter currents, and the only energy which has to be supplied is that equivalent to the non-recoverable fraction of the heat stream and the heat lost through the insulation.

By definition, the separation coefficient is

$$\alpha = \frac{x_e}{1-x_e}\frac{1-y_e}{y_e}, \tag{1}$$

where x_e and y_e are the equilibrium concentrations of deuterium in A and B respectively. At low concentrations

$$\alpha = x_e/y_e. \tag{2}$$

If the number of stages in the two columns is high, the maximum transfer occurs at the start of the process and it can be assumed that at the ends of the columns we have equilibrium between A and B at concentrations x_0 and y', and x' and y'. Thus $y' = x_0/\alpha_1$ (cold column) and $y' = x'/\alpha_2$ (hot column), from which

$$x' = x_0\alpha_2/\alpha_1. \tag{3}$$

Since $\alpha_1 > \alpha_2$, $x' < x_0$ and deuterium accumulates in the system. The greatest concentration will evidently be reached in the lower part of the cold column I and in the upper part of the hot column II, and P mole h^{-1} of substance A with deuterium concentration x_e are removed from these points. Eqn.(3) shows that the concentration is more readily achieved the greater the difference between the separation coefficients.

It is possible to extract $(x_0 - x')$ moles of deuterium from each mole of the stream of substance A passing through the system of columns. If we take the value of x' from Eqn.(3), it is possible to extract $x_0(1 - \alpha_2/\alpha_1)$ moles of deuterium. The factor $(1 - \alpha_2/\alpha_1)$ is the maximum possible degree of extration:

$$\varphi_{max} = \frac{\alpha_1-\alpha_2}{\alpha_1}. \tag{4}$$

The actual degree of extraction φ is a fraction of the maximum φ_{max}. The degree of extraction of deuterium can be increased by increasing the temperature difference between the hot and cold columns. All the extracted deuterium is taken from the stream of substance A.

The process taking place in the dual-temperature system may be represented by plotting x vs. y: the equation for the equilibrium line of the cold column is

$$x = \alpha_1 y, \tag{5}$$

and that for the hot column is

$$x = \alpha_2 y. \tag{6}$$

The equations for the actual concentrations may be derived from the material balance. For the cold column we have

$$L_A(x - x_0) = L_B(y - y'). \tag{7}$$

Dividing by L_A and denoting L_B/L_A by λ, we obtain

$$x = \lambda y - \lambda y' + x_0. \tag{8}$$

For the hot column we have

$$L_B/(L_A - P) = \lambda',$$

and

$$x = \lambda' y - \lambda' y' + x'. \qquad (9)$$

In the dual-temperature process, we have two equilibrium-concentration lines and two operating-concentration lines (Fig.3). Since the deuterium concentrations x_e (A) and y_e (B) in the currents are the same for both columns, the operating lines should intersect at S. If no product is removed, the two operating lines merge into a single line.

The possibility of changing the position of the operating lines is restricted by the space between the two equilibrium lines. Since the position of the operating lines is determined by the stream ratios λ and λ', the actual change in the stream ratio is also restricted. We have

$$\alpha_1 > \lambda \geqslant \lambda' > \alpha_2, \qquad (10)^*$$

that is in the dual-temperature process it is necessary to maintain a definite molar stream ratio.

The physical significance of this restriction is that the dual-temperature counter current process of concentration requires that a sufficiently high fraction of the deuterium which enters stream A from the stream B in the cold column *I* is transferred back to stream B in the hot column *II*. Since the separation factor at temperature T_2 is much greater than unity, and since the deuterium concentration in stream A when equilibrium has been reached exceeds that in stream B, the transfer of deuterium to stream B is greatly facilitated by a decrease in stream A, that is by an increase in the stream ratio λ to values of λ greater than α_2. The stream ratio λ must not be made greater than α_1, however, since this leads to breakdown of the process of concentration in the cold column *I*. At a stream ratio less than α_2 or greater than α_1, it is possible to obtain only a very slight enrichment, which cannot be increased significantly by increasing the height of the column[52]. The influence of the stream ratio on the degree of enrichment is shown in Fig.4.

The product may be removed in two ways: in the first method (Fig.2) the product is removed and is not returned to the system; in the second method an equal quantity, P mole h^{-1}, of stream A, with concentration x'_e less than x_e, is supplied to column II. The dual-temperature cascade process of concentration (Fig.5) consists essentially, of removal by the second method in the first two stages and removal by the first method in the third stage. It is important in this process to remove the product by the second method from both streams simultaneously (Fig.6). This avoids changing the stream ratio as a result of removal from only one stream, decreases slightly the time taken for the steady state to be reached in the cascade of dual-temperature columns, and reduces the heat-exchange apparatus in the subsequent stages. A number of possible methods of carrying out the dual-temperature process have been described by Roth[45] and in some French patents[53,54].

The principle of the dual-temperature method for preparing heavy water has been described in a number of papers[12,19-25,30,31,35,55-57]. The details of the dual-temperature separation have been examined by Bier[52,58], Rozen[59,60], and others[57,61,62]. Approximate calculations[59-61] for the dual-temperature process suggest that the separation coefficient can be taken as $\sim\sqrt{\alpha_1/\alpha_2}$. The remaining calculations can then be carried out as for the usual cascade-concentration schemes.

* The restriction in the stream ratio [Eqn.(10)] does not apply to operation according to the scheme illustrated in Fig.1.

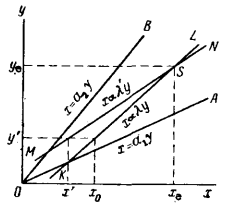


Fig. 3. Plot of x vs. y for the dual-temperature process. OA is the equilibrium line of the cold column, OB the equilibrium line of the hot column, KL the operating line of the cold column, and MN the operating line of the hot column.

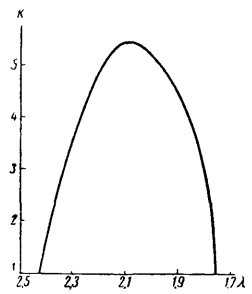


Fig. 4. Dependence of the enrichment (K) on the stream ratio (λ), from Savannah River data.

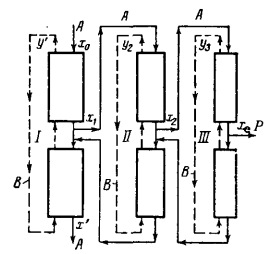


Fig. 5. Dual-temperature columns connected in a cascade with removal of product from stream A. I) First stage; II) second stage; III) third stage; P) removal of product.

When choosing operating temperatures, allowance must be made for the fact that although increase in temperature accelerates the isotopic exchange, the temperature coefficient of the equilibrium constant (or of the separation factor) decreases with increase in temperature, so that to obtain the same degree of extraction of deuterium it is necessary to extend the interval between the operating temperatures of the hot and cold columns. Low temperatures, on the other hand, reduce the activity of the catalysts which

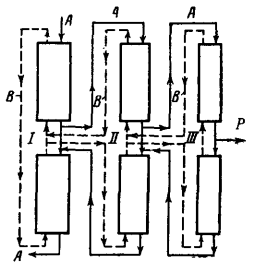


Fig. 6. Dual-temperature columns connected in a cascade with removal of product from both streams. I) First stage; II) second stage; III) third stage; P) removal of product.

are often used to accelerate the isotopic exchange. For water-cooling to be possible, the lower temperature should not be less than 25–30°. The temperature of the hot column should not be too high, since this increases the consumption of high-pressure steam. In the choice of operating temperatures allowance should be made for all the characteristics of the substances in the separation system. The pressure should be as high as possible for a given system of substances, used for deuterium exchange, in order to decrease the volume of gas to be pumped over, to increase the efficiency, and to reduce the total volume of the apparatus. The use of very high pressure, however, introduces technical difficulties and leads to high capital expenditure.

The plot of x vs. y for the dual-temperature process (Fig.3) shows that by changing the stream ratio we can vary the number of theoretical separation stages of the hot and cold columns to obtain the same degree of deuterium enrichment. In the choice of the number of stages of hot and cold columns n_h and n_c account should be taken of the height of the equivalent theoretical stage of hot and cold columns h_h and h_c, so that the total height (and volume) of the columns shall be a minimum, i.e. $(n_h h_h + n_c h_c)$ shall have a minimum value.

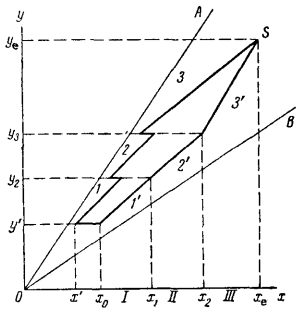


Fig. 7. Plot of x vs. y for the cascade of dual-temperature columns illustrated in Fig. 5. [60]. OA is the equilibrium line of the cold column, OB the equilibrium line of the hot column, 1 and 1' are the operating lines of the first stage, 2 and 2' the operating lines of the second stage, and 3 and 3' the operating lines of the third stage.

The division of the total enrichment throughout the stages of the cascade must be made in such a way that the number of stages of the cascade does not exceed 2–4, since a higher number gives no advantage in reducing the total volume of the apparatus. The plot of x vs. y for the cascade in Fig.5 is given in Fig.7. [60]

DEUTERIUM-EXCHANGE SYSTEMS

The choice of substances A and B is influenced by the following considerations. The separation factor should be as high as possible, and should change significantly with change in temperature. The substances should be readily separable from one another, should be chemically stable, and should not be decomposed by repeated circulation under changing temperature conditions. They should contain the smallest possible "ballast" of non-exchanging atoms and should have the smallest possible corrosive action on the material of the apparatus. It is desirable that the isotopic exchange between the substances should take place sufficiently rapidly to make the use of a catalyst unnecessary.

An approximate calculation of unknown separation factors for many pairs of substances can be carried out by a method developed by Varshavskii and Vaisberg [63–65]. Data for the separation factors, their temperature dependence, and the degrees of extraction for the most promising systems in the range 20°–100° are given in Table 2.

TABLE 2. Comparison of different systems of deuterium-exchange substances.

System	α_{20}/α_{100}	$\sqrt{\alpha_{20}/\alpha_{100}}$	φ_{max}	System	α_{20}/α_{100}	$\sqrt{\alpha_{20}/\alpha_{100}}$	φ_{max}
H_2–NH_3	1.51	1.23	0.34	H_2O–AsH_3	1.20	1.09	0.13
H_2–H_2O	1.48	1.22	0.32	H_2O–H_2Se	1.27	1.12	0.21
H_2O–PH_3	1.14	1.07	0.12	H_2O–HBr	1.33	1.15	0.25
H_2O–H_2S	1.26	1.12	0.18	H_2O–HI	1.41	1.19	0.29
H_2O–HCl	1.27	1.13	0.21				

It is usually convenient to choose water as one of the substances, since it provides an almost inexhaustible source of deuterium and it is readily available.

The highest extraction of deuterium is obtained with the water–hydrogen, water–hydrogen halide, and ammonia–hydrogen systems. For practical reasons, however, it is most convenient to use the water–hydrogen sulphide system, which is widely employed. The principal systems which have been proposed for use in the dual-temperature process are examined below.

Water–Hydrogen

This system was the first to be used for the dual-temperature process. The temperature dependence of the equilibrium constant (which in this case is equal to the separation factor) for the reaction

$$H_2O_{vap} + HD \rightleftarrows HDO_{vap} + H_2 \qquad (I)$$

is given in Table 3.[19]

TABLE 3. Temperature dependence of the separation factor for exchange reaction (I).

Temp., °C	50	60	70	100	200	300	600	700
$\alpha(K)$	3.05	2.92	2.83	2.56	1.98	1.69	1.30	1.24

It is possible to obtain a maximum degree of extraction, $\varphi_{max} = 0.49$, by using operating temperatures of 100° and 600°. The scheme proposed initially by Harteck and Suess is illustrated in Fig.1. An experimental assembly was built at Leuna in 1943-1944 for the initial enrichment of water to 1% D_2O. The system consisted of 10 pairs of cold and hot contact assemblies, packed with a catalyst, and was intended to operate at 100° and 600°, [12,19,36] but it was destroyed during an air raid. The production of heavy water by this scheme requires the expenditure of large quantities of heat and energy, since repeated evaporation and condensation are necessary; in each apparatus there is a single flow of hydrogen and steam, and the cold and hot stages work at different pressures.

Cerrai and coworkers [19,24,66] developed an improved version of the dual-temperature process with water and hydrogen (Fig.8). The water enters the enrichment column *I*, consisting of alternating layers of catalyst and bubble-cap trays, analogous to the Trail column [15] and then passes to a stripping column *II* consisting of bubble-cap trays only, after which it is rejected. The temperature of columns *I* and *II* is fairly low (80°). A mixture of water vapour and hydrogen flows in the opposite direction to that of the water and passes from the upper part of column *I* to column *III*, which is filled with catalyst and operates at a high temperature (600°). The deuterium concentration in the water increases in column *I* as a result of the catalysed isotopic exchange between water vapour and hydrogen at low temperatures and the phase exchange between water and water vapour. The product can be removed from the lower part of column *I*. In column *II*, the phase exchange between water and water vapour leads to a decrease in the deuterium concentration in the water, since the water vapour entering the lower part of column *II* is poorer in deuterium as a result of the catalytic isotopic exchange with hydrogen at high temperature in column *III*. This arrangement reduces slightly the quantity of heat used, but this is still fairly high. Each stage cannot give an enrichment greater than α_1/α_2.

The scheme illustrated in Fig.2 is advantageous from considerations of capital and operating costs. Reaction (I) takes place in the gaseous phase, however, so that it is impossible to set up continuous counter current conditions. To carry out the exchange reaction in a column apparatus it is necessary to make use of the exchange between hydrogen and liquid water,

$$H_2O_{liq} + HD_{gas} \rightleftarrows HDO_{liq} + H_{2gas}, \qquad (II)$$

for which the equilibrium constants are given in Table 4.[19]

The difficulty in carrying out reaction (II) lies in the lack of a suitable catalyst, since liquid water rapidly decreases the activity of ordinary catalysts. It is convenient to use as catalysts compounds which are soluble in water or which can be dispersed in water, as in the scheme developed by Becker (Fig.9)[19]: here the water circulates in a closed circuit and the hydrogen is the source of deuterium, so that the efficiency of the method is limited by the quantity of available hydrogen. This restriction can be eliminated by introducing another supplementary column *III* for exchange between water and hydrogen at 250°, but this technique is not economic.

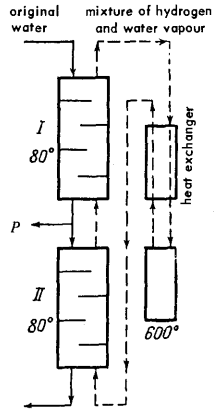


Fig. 8. Cerrai's scheme for dual-temperature exchange between water and hydrogen. I) Cold column for phase and catalytic isotopic exchange; II) cold column for phase exchange; III) hot column for catalytic isotopic exchange; *P*) removal of product.

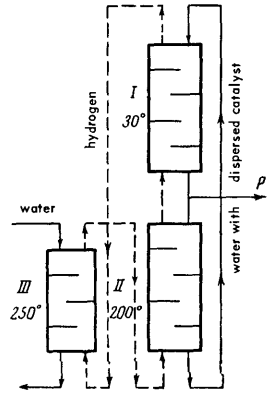


Fig. 9. Dual-temperature isotopic exchange between water and hydrogen with a dispersed catalyst. I) Cold column; II) hot column; III) regenerative hot column; *P*) removal of product.

TABLE 4. Temperature dependence of the separation factor of exchange reaction (II).

Temp., °C	0	25	50	75	100	125
$\alpha(K)$	4.69	3.87	3.37	2.99	2.69	2.47

To increase the degree of extraction of deuterium, Becker suggested reducing the temperature of the cold column from 80° to 30°–40°, while leaving the temperature of the hot column at 200°:[57] in this case $\varphi_{max} = 0.44$. To reduce the volume of gas to be pumped over and increase the efficiency, an operating pressure of 200 atm was chosen. The use of hydrogen as raw material (without the supplementary column *III*) gives material streams per unit of product approximately α times smaller, since the hydrogen leaving column *III* after exchange with water has a lower deuterium content than natural hydrogen (the equilibrium constant favours increase in the deuterium concentration in the water, not in the hydrogen). It should be borne in mind, however, that ordinary technical hydrogen has a slightly lower deuterium content (by 10–20%) than natural hydrogen.

TABLE 5. Temperature dependence of the separation factor for exchange between ammonia and hydrogen.

Temp., °C	−50	0	25	100
α	6	4.56	3.88	2.73

Becker made a detailed study of the catalyst (consisting of platinum on a support of wood charcoal dispersed in water) which he proposed for the liquid-phase exchange [19,57,67]. The platinum content varies over wide limits but is normally 7 g per litre of water, dispersed on a tenfold excess of wood charcoal. The experiments were carried out with sieve plates under conditions similar to those used in industrial production. According to Becker's calculations, the specific volume of the sieve column should be 23 m^3 ton^{-1} D_2O and the platinum consumption 16 kg ton^{-1} D_2O per year. The energy required for heating was estimated as 0.94×10^6 kcal kg^{-1} D_2O for a heat-exchanger efficiency of 75%, and the energy required for mixing was estimated as 200 kWh kg^{-1} D_2O. A number of French workers have also studied the catalyst for liquid-phase exchange[45,68].

The firm of Degussa (Western Germany) recently decided to construct an experimental apparatus to prepare ~ 1 ton of heavy water per year by dual-temperature exchange between water and hydrogen with dispersed platinum as catalyst[69–76].

Ammonia–Hydrogen

The possibility of using the isotopic exchange between ammonia and hydrogen for preparing heavy water by the dual-temperature method was examined in the USA in 1942[33a]. The separation coefficients of this system have a marked temperature dependence (Table 5).[77] When the operating temperatures are 25° and 100°, $\varphi_{max} = 0.30$, that is, the system has a high degree of extraction at a comparatively small difference between the temperature of the two columns. The scheme is illustrated in Fig.10. The supplementary column *III* is not essential, since the process is then complicated by the need to extract the ammonia from the drainage water, but it eliminates the dependence on a large-scale source of hydrogen. The study of this system was discontinued in 1943 because of the absence of a suitable catalyst for the isotopic exchange.

In 1950 it was found that potassamide is a convenient catalyst for the isotopic exchange between ammonia and hydrogen. This exchange was studied in detail by Bigeleisen et al.[78,79]. At a potassamide concentration approximately 10^{-3} M, the rate of exchange is controlled by chemical factors and depends on the concentration of the amide ion. At higher concentrations, approximately 10^{-1} M, the rate of exchange is independent of the concentration and is determined by diffusion. The slowest diffusion process is apparently the transfer of hydrogen across the layer of liquid at the liquid–gas interface. When the gas was bubbled through the liquid in an apparatus with bubble-cap trays (plates), the Murphree plate efficiency amounted to 0.5–9%. French workers[45] who studied the kinetics of exchange in packed columns and on sieve plates obtained higher efficiency values; they also showed that potassamide is highly sensitive to the presence of moisture and oxygen.

Using data on the exchange equilibrium between ammonia and hydrogen, the marked temperature dependence of the separation factor, and the catalytic properties of potassamide, the English firm constructors John Brown Ltd. developed a project for preparing 27 tons of heavy water per year. The initial process of concentration to 0.4% D_2O was carried out by a combination of single-temperature and dual-temperature exchange between hydrogen and ammonia[80–84]. The initial enrichment is illustrated in Fig.11. In column *I* single-temperature exchange takes place between the hydrogen of a nitrogen–hydrogen mixture and ammonia containing potassamide catalyst, and the deuterium content of the ammonia is increased by a factor of 5. In columns *II* and *III*, working at -40° and 100°, dual-temperature exchange takes place between the ammonia and hydrogen, and the deuterium content of the ammonia leaving the cold column *II* is increased by a factor of 23. The impoverished ammonia passes from the hot column *III* to column *I* and then to cold column *II*. The operating pressure in the system is 250 atm. The enriched ammonia is removed and passed to a distillation cascade of 7 columns. The distillation of the ammonia increases the deuterium concentration to 75%. The final process of concentration to 99.8% is carried out in a Kuhn column irrigated with water which is enriched in deuterium by exchange with the ammonia from the distillation cascade. Naturally, this assembly can only be set up in a nitrogen fetiliser plant. This would reduce capital expenditure, since standard equipment is used. An advantage of the method is that it is possible to use the nitrogen–hydrogen mixture without the expensive purification which is necessary when low-temperature distillation is used. A significant disadvantage is the large volume of apparatus working under high pressure. According to the project data, the method can produce heavy water at a cost of 47.6 dollars per kg[81–84].

A study has been made in the USA of the possibility of

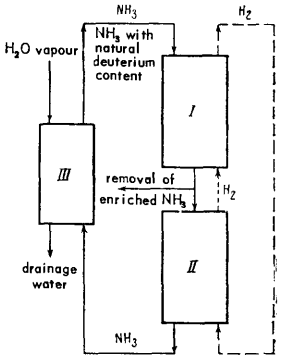


Fig. 10. Dual-temperature exchange in the ammonia – hydrogen system. I) Cold column; II) hot column; III) regenerative colomn.

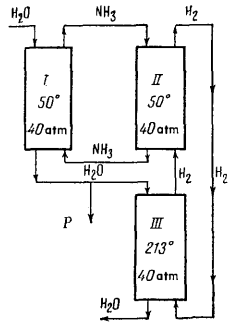


Fig. 12. Dual-temperature process for the water – – ammonia – hydrogen system. I) Cold column for exchange between water and ammonia; II) cold column for exchange between hydrogen and ammonia; III) hot column for exchange between water and hydrogen; P) removal of product.

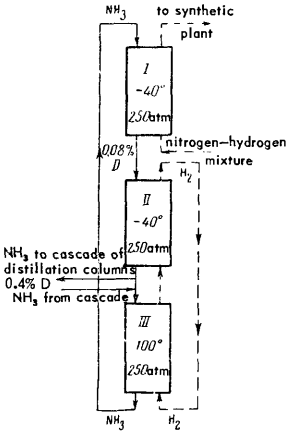


Fig. 11. Preparation of heavy water by a combination of single-and dual-temperature exchange between hydrogen and ammonia. I) Cold colum for single-temperature exchange; II) cold column for dual-temperature exchange; III) hot column for dual-temperature exchange.

using a three-component water–ammonia–hydrogen system, which eliminates the dependence on a large-scale source of hydrogen[33b]. The process is illustrated in Fig.12. In column *I* the water is enriched in deuterium by exchange with deuterium-rich ammonia; the product is removed along the line *P*, and the greater part of the water stream enters column *III*, in which hydrogen extracts deuterium from the water at high temperature. The hydrogen leaving column *III* undergoes exchange with ammonia in the cold column *II*. This is thus a modification of the water–-hydrogen exchange process, rather than a modification of the ammonia-hydrogen exchange process. All the extracted deuterium comes from the water. The presence of the ammonia does not alter the degree of extraction of deuterium, but makes it possible to replace the difficult counter current exchange between water and hydrogen at low temperatures by the easier exchange between ammonia and hydrogen. The capital expenditure required by this scheme, however, makes it uneconomic.

Water–Hydrogen Sulphide

The chief advantage of the water–hydrogen sulphide system is the high rate of exchange, which makes it possible to use ordinary columns without a catalyst. The high rate of exchange is due to the ionic mechanism of the exchange, a consequence of the ionic dissociation of hydrogen sulphide in water. By increasing the pressure in the system, it is possible to reduce the concentration of water vapour in the hot gas, to decrease the volume of the columns, and to lower the energy required for transporting the gas. The upper pressure limit is 18–20 atm, however, since higher pressure greatly increases the solubility of hydrogen sulphide in water and its condensation in the cold column can occur at 23 atm. Harteck has suggested using exchange between water and liquid hydrogen sulphide[35], but this is inconvenient since the specific gravity of liquid hydrogen sulphide is close to unity, so that it is difficult to set up counter current conditions in the liquid–liquid system. It is possible, moreover, that the rate of exchange between water and liquid hydrogen sulphide is much smaller than that between water and gaseous hydrogen sulphide.

The separation factor for the hydrogen isotopes in the exchange reaction

$$H_2O_{liq} + HDS_{gas} \rightleftarrows HDO_{liq} + H_2S_{gas} \qquad (III)$$

has been determined by a number of workers[19,45,51,85–88]. The value is usually found by a static method: when equilibrium has been reached, the water and hydrogen sulphides are separated from one another at the equilibrium temperature and analysed for deuterium.

When exchange is carried out under ordinary conditions, the main reaction (III) is complicated by other exchange processes, due to the solubility of hydrogen sulphide in water and the presence of water vapour in the hydrogen sulphide:

$$H_2O_{gas} + HDS_{gas} \rightleftarrows HDO_{gas} + H_2S_{gas}, \quad (IV)$$

$$H_2S_{soln} + HDS_{gas} \rightleftarrows HDS_{soln} + H_2S_{gas}, \quad (V)$$

$$H_2O_{liq} + HDO_{gas} \rightleftarrows HDO_{liq} + H_2O_{gas}. \quad (VI)$$

The separation factor for reaction (IV) can be calculated from the formula proposed by Bigeleisen[86].

$$\alpha = 1.051 e^{\frac{218 \pm 2}{T}}. \quad (11)$$

The applicability of the Bigeleisen formula was confirmed by Gemmell, MacClair and Carrick[79]. To calculate α_3 we will use the following relationship between α_3 and α_4:

$$\alpha_{(3)} = \alpha_{(4)}/f. \quad (12)$$

The relative volatility f is

$$f = \frac{HDO_{gas} H_2O_{liq}}{H_2O_{gas} HDO_{liq}} \quad (13)$$

Eqn.(12) can be used to calculate the separation factors for the hydrogen isotopes in the exchange between gaseous hydrogen sulphide and liquid water at different temperatures.

The separation factor values obtained by various workers are given in Table 6. The temperature dependence of the separation factor for the exchange between water and hydrogen sulphide is much less marked than that between water and hydrogen, so that for operating temperatures of 20° and 100°, $\varphi_{max} = 0.18$, which is approximately half the value for exchange between water and hydrogen.

Spevack[51] and Weiss[35] suggested using the effective separation factors β for technological calculations because of the solubility of gaseous hydrogen sulphide in water and the presence of water in the hydrogen sulphide. Spevack[51] suggested determining β from the formula

$$\beta = \frac{(1+H)(S+\alpha_{(4)})}{f(1+S)(1+\alpha_{(4)})}, \quad (14)$$

where H is the moisture content of the gas phase in moles of H_2O per mole of H_2S, S the solubility of hydrogen sulphide in water in moles of H_2S per mole of H_2O, and f the relative volatility given by Eqn.(13).

Values of the effective separation factors at 18 atm are given in Table 7.[35] In the calculation of the dual-temperature process from a plot of x vs. y it is convenient to use the values of β_1 and β_2.

The kinetics of the isotopic exchange between water and hydrogen sulphide have been studied by French workers[45], who showed that the rate is independent of the concentration of dissolved hydrogen sulphide when 50% of the equilibrium concentration has been reached. Their study of the corrosion of the materials used in the apparatus by hydrogen sulphide is of particular interest[45].

Weiss has given a detailed discussion of the optimum conditions for the dual-temperature process with the water–hydrogen sulphide system[35]. He suggests keeping the temperature of the cold column at 30° in order to prevent precipitation of solid hydrogen sulphide hydrate, $H_2S.5H_2O$, and allow for the fact that the temperature of the coolant water in the summer months is 20°. He suggests that the temperature of the hot column should be 120°, which is a compromise between reduction of the heat consumption and increase in the degree of extraction of deuterium. Weiss also discusses the choice of optimum gas and liquid streams, number of stages, and division of the total enrichment among the stages of the cascade. An electronic computer has been used in England to find the optimum conditions for the exchange between water and hydrogen sulphide, and analogous results were obtained: optimum temperatures are 30° and 120°–130° and optimum pressure 20 atm.[89]

The chief disadvantage of the water–hydrogen sulphide system is the extensive corrosion of constructional materials by hydrogen sulphide, necessitating expensive stainless-steel apparatus. The dual-temperature exchange between water and hydrogen sulphide was first studied by Geib in Leuna during the second world war[12,19,90]. About the same time, a study of this system was begun in the USA[15,51], but the method was not then established on an industrial scale because of the expected extensive corrosion of the constructional materials.

The dual-temperature exchange between water and hydrogen sulphide was first carried out on an industrial scale in the Soviet Union. A large-scale industrial plant was constructed in the USSR in 1946–49, and this is still operating successfully. Somewhat later the dual-temperature exchange between water and hydrogen sulphide was also used in the USA. During 1951–1953 the firm of Dupont, under contract to the AEC, constructed two large-scale plants for the production of heavy water, in Dana (Indiana) and on the Savannah River (South Carolina). The total productive capacity of the two plants is ~ 800 tons of heavy water per year[57,91]. The construction of the Dana

TABLE 6. Temperature dependence of the separation factor for exchange between water and hydrogen sulphide.

Temperature, °C	0	5	10	25	50	100	150	Reference
Separation factor				2.37				85
		2.52	2.48	2.34		1.92		19,24,50
	2.55			2.35	2.17	1.95	1.80	51
				2.35				35,88
	2.52		**2.39**	2.26	2.09	1.86	1.71	45

TABLE 7. Effective separation factors for exchange between water and hydrogen sulphide at 18 atm.

t°C	$\alpha_{(4)}$	$\alpha_{(3)}$	P_{H_2O}/P_{HDO}	H	S	β	t°C	$\alpha_{(4)}$	$\alpha_{(3)}$	P_{H_2O}/P_{HDO}	H	S	β
10	2.27	2.47	0.92	0.001	0.045	2.40	75	1.97	2.05	0.96	0.027	0.014	1.98
20	2.21	2.38	0.93	0.002	0.036	2.33	100	1.88	1.94	0.97	0.074	0.010	1.81
30	2.16	2.31	0.93	0.003	0.030	2.27	120	1.83	1.86	0.98	0.144	0.008	1.68
50	2.06	2.18	0.95	0.009	0.020	2.13	140	1.78	1.80	0.99	0.280	0.007	1.53

plant cost 100 million dollars, and that of the Savannah River plant 164 million dollars[40,57,92,93]. These two plants produced such a large quantity of heavy water that at the beginning of 1957 the AEC decided to close temporarily the Dana plant[94-98]. The Dana plant was chosen since the equipment in it was made of less corrosion-resistant material and the cost of the heavy water produced there was higher than that in the Savannah River plant. Later, the Dana plant was transferred to the Chemical Corps of the US Army for the production of a new chemical product[99,100] The Savannah River plant is still operating and its maximum productive capacity is 450 tons of D_2O per year[40].

Dual-temperature exchange between water and hydrogen sulphide is used in the Savannah River plant for the initial process of concentration from the natural level to 15% D_2O. According to recent reports, the initial process of concentration in this plant is carried out by a two-stage cascade of dual-temperature columns. The operating temperatures

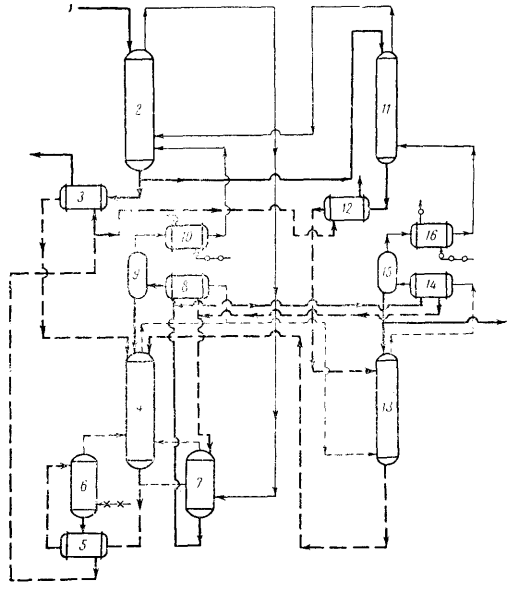


Fig. 13. Preparation of heavy water by dual-temperature exchange between water and hydrogen sulphide in the Savannah River plant (USA). 1) Feed water after purification; 2) cold column of first stage; 3) shell-and-tube liquid – liquid heat exchanger; 4) hot column of first stage 5) shell-and-tube liquid – liquid heat exchanger; 6) 2 m packed column for the reduction of hydrogen sulphide content to one millionth; 7) direct mixing humidifier (heat exchanger); 8) gas – liquid heat exchanger; 9) separator; 10) additional gas – liquid heat exchanger; 11) cold column of second stage; 12) shell-and-tube liquid – liquid heat exchanger; 13) hot column of second stage; 14) gas – liquid heat exchanger; 15) separator; 16) additional gas – liquid heat exchanger. Thick line – cold process water; thick broken line – hot process water; thin line – cold circulating hydrogen sulphide; thin broken line – hot circulating hydrogen sulphide; –o–o coolant water; –×–×– -heating steam.

are 30° and 120–130°, the pressure in the system is 17 atm, and the molar ratio of the hydrogen sulphide and water streams is 2.1 : 1. The initial process of concentration is illustrated in Fig. 13. One quarter of the stream of water and hydrogen sulphide from the first stage is passed to the second stage. The product is removed from the water and hydrogen sulphide streams simultaneously, and this minimises the heat-exchange apparatus required in the second stage of the cascade. The arrangement of the streams in the initial process of concentration ensures the most complete use of the heat of the streams of hydrogen sulphide and the water by direct heat exchange in the humidifier 7 and indirect heat-exchange in the shell-and-tube heat-exchangers. Live steam is blown through the outlet water to reduce the hydrogen sulphide content to one millionth.

The exchange assembly consists of a 30 m high column with bubble-cap trays; the diameter of the first stage is 3.3–3.6 m, and that of the second stage 2 m. A combined system in which the columns are connected in a cascade is used, and the initial concentration section is broken down into separate units, each consisting of two columns [a cold and hot column in the first stage and four columns (two cold and two hot) in the second stage]. This combined system facilitates servicing and repairs and makes it possible to shut down the separate columns[101,102].

The two-stage cascade for the initial process of concentration is used in the Savannah River plant, rather than the five-stage cascade as in the Dana plant, in an attempt to simplify the process and reduce the number of control points. The experience of seven years' operation has shown that the process of concentration is not greatly affected by variations in the stream ratio within +1%.

The corrosion problem was solved by using ordinary steel clad with stainless steel. The possibility of adding corrosion inhibitors, (in particular amines or ammonia), to the feed water has not yet been fully studied.

The following are the requirements for the initial process of concentration, per kg of heavy water: 40 tons of feed water, 150 tons of circulating hydrogen sulphide, 125 tons of coolant water, 6 tons of heating steam at 18.5 atm, and 630 kWh of electrical energy. The degree of extraction of deuterium from the feed water is ~ 18%.

Further concentration to 90–98% D_2O is carried out by fractional distillation in vacuo in two cascades, each consisting of six columns with bubble-cap trays. The final concentration to 99.8% is carried out in an electrolytic assembly consisting of 150 cylindrical baths. The capital expenditure on the initial concentration was 114 million dollars, that on the distillation assembly 2.5 million dollars, and that on the electrolytic assembly 1.5 million dollars[40,93]. The investment per unit of product is 362 dollars per year per kg of D_2O and the operating cost is 30 dollars per kg of D_2O.[93,103].

Plants using the dual-temperature water–hydrogen sulphide system have enabled the USA not only to satisfy all her internal demand for heavy water, but also to export in at a price of 62 dollars per kg. Up to the end of 1958 ~ 400 tons of heavy water had been sold to various countries, including England, France, India, etc.[104,105]. As a result of fluctuations in the demand for heavy water, the Savannah River plant decreased production of D_2O in October 1958 by two thirds[106]. To increase the demand, the US Atomic Energy Commission offered to lend heavy water at 4% per annum[47-49]. India was the first country to accept and borrowed 15 tons[107].

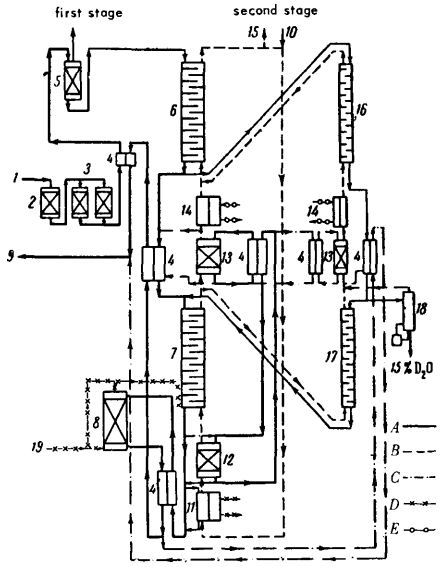


Fig. 14. German experimental two-stage assembly for preparing D_2O by dual-temperature exchange between water and hydrogen sulphide. 1) Fresh water supply; 2) 2) gravel filter; 3) ion-exchange water purifier; 4) heat exchanger; 5) degassing column; 6) cold column of first stage; 7) hot column of first stage; 8) apparatus for distilling off hydrogen sulphide; 9) removal of spent water; 10) supply of hydrogen sulphide; 11) heater; 12) saturator; 13) drier; 14) condenser; 15) removal of hydrogen sulphide for purification; 16) cold column of second stage; 17) hot column of second stage; 18) distillation apparatus for product; 19) steam supply. *A* – process water; *B* – hydrogen sulphide; *C* – process water used as heat-exchange medium; *D* – heating steam; *E* – coolant water.

The preparation of heavy water by dual-temperature exchange between water and hydrogen sulphide, often referred to simply as the hydrogen sulphide method, has attracted considerable attention in other countries interested in producing heavy water for themselves, particularly Western Germany, where laboratory studies have been completed and the construction of industrial plant has begun.

After considerable study and experiment for 2–3 years, the firm of Pintsch-Bamag constructed an experimental plant to produce 0.5 ton of heavy water per year by the dual-temperature exchange between water and hydrogen sulphide [47,35,73,90,108]. The process is illustrated in Fig. 14. [35] The total enrichment factor of 1000 is achieved in a two-stage cascade: the first has an enrichment factor of 16, the second of 64. The hot and cold columns of both stages of the cascade are divided into 4 columns in series, to reduce the total height. The temperature of the cold columns is 30°, that of the hot columns 120°, and the pressure 18–20 atm. The flow rates in the first stage are 2.17 tons h^{-1} of water and 8.8 tons h^{-1} of hydrogen sulphide; the molar stream ratio is 1 : 2.14. The material streams in the second stage are 16 times smaller. The number of theoretical separation stages in both stages of the cascade is 213.

It has recently been reported that the firm of Pintsch-Bamag has undertaken the construction of an experimental plant [109,110], scheduled for completion by the beginning of 1960, [111–113] in Batzbach [48], close to the existing plant of the firm Farbwerk Hoechst [110]. The construction of this experimental plant is the first step in providing Western Germany with large-scale plants for the production of heavy water by the hydrogen sulphide method [108]. A plant for the production of 40 tons of D_2O per year is now planned [111,112,114]. It is proposed to achieve an initial concentration of up to 15% D_2O by dual-temperature exchange in a three-stage cascade. The estimated cost of the plant is 12 million dollars [115].

Various firms, including SOD, a public company formed in France to produce heavy water, have shown interest in the dual-temperature exchange between water and hydrogen sulphide [45,116,117]. An experimental one-stage assembly was built in Lacq for the initial concentration of heavy water by a two-temperature method using natural gases containing up to 15% of hydrogen sulphide, in columns 0.3 m in diameter and 6 m high filled with 15 × 15 Raschig rings: the temperature of the cold column is 30°, that of the hot column 120°, and the pressure is 15 atm. It is calculated that 17 tons of heavy water per year can be produced in Lacq by preliminary enrichment of the water by exchange with hydrogen sulphide [45,117].

Sweden has planned to produce heavy water for use in power reactors [118]. The "ASEA" concern has plans to build a large-scale plant to produce 25 tons of D_2O per year, increasing to 100 tons per year [119,120]. The initial estimate of the cost of construction is 4–6 million dollars and the estimated cost of the heavy water is approximately two thirds of the present American price [120]. 300 000 dollars have been assigned to the project for 1959. [121] An experimental plant comprising columns 1 m in diameter and 15 m high has been set up in Kvarntorp to provide experience [4,122].

Plans have been made in Spain for laboratory studies and the construction of an experimental plant to produce heavy water by the hydrogen sulphide method, in order to gain experience before constructing a large-scale plant [123,124].

The Organisation for European Economic Cooperation has considered a plan to build a common European plant in Iceland to produce 500 tons of heavy water per year by the hydrogen sulphide method. The estimated cost of the plant was 200 million dollars and it was expected that the price of the heavy water would not be greater than the present American one [35,125,126]. England, and possibly the USA, were prepared to take part in the construction of the plant. After more detailed discussion it was decided to build initially a plant in Iceland able to produce 100 tons of D_2O per year [48,127]. The cost of construction will be 36 million dollars.

Other Systems

Urey has suggested the use of a liquid mercaptan RSH in place of gaseous hydrogen sulphide in the dual-temperature process [128]. This would eliminate corrosion, reduce the energy required for transporting the exchange materials, and facilitate the recovery of heat in the opposed streams.

Studies directed by Urey and carried out by Hutchison and Gillies [33b,129] on the possibility of using isopropanethiol showed, however, that the rate of isotopic exchange is insufficient. The firm of Pintsch-Bamag studied the

TABLE 8. Temerature dependence of the separation factor for the exchange between water and hydrogen halides.

Temperature, °C		0	25	100	125	227
System	H_2O—HCl	2.87	2.51	1.98	1.87	1.59
	H_2O—HBr	3.57	3.07	2.34	2.17	1.79
	H_2O—HI	4.55	3.80	2.78	2.56	2.06

possibility of using dithioethyleneglycol in a dual-temperature process[18,35], and found that the temperature dependence of the separation factors satisfies the requirements of the dual-temperature method, and that the rate of exchange is slightly higher than the rate of the extraction processes in the liquid–liquid system. On the basis of these data, plans were made for a plant to produce 36 tons of D_2O per year. However, calculations for this plant showed that because of the large volume of the exchange apparatus, the high cost of the dithiol used in the initial charging, and the loss of dithiol in the drainage water, the construction of the plant was inadvisable, since the capital expenditure and energy consumption would be approximately double that when hydrogen sulphide is used as circulating material[35].

The possibilities of a two-temperature process with the phosphine–water system were studied by Weston and Bigeleisen,[130,131] who found, however, that the exchange rate was too low.

Augood studied the possibility of using hydrogen halides as exchange substances[16]. The temperature dependence of the separation coefficients is favourable (Table 8) but the hydrogen halides are very soluble in water, which makes their recovery from the drainage water difficult, and have a marked corrosive action; these features make them unsuitable.

Taylor has suggested using the three-component cyclohexane–benzene–hydrogen system[33b,132] for the dual-temperature preparation of heavy water. The process is based on the fact that in the presence of a catalyst the equilibrium

$$C_6H_6 + 3H_2 \rightleftarrows C_6H_{12}\,, \qquad \text{(VII)}$$

is displaced towards the formation of cyclohexane at 100° and towards the formation of benzene at 300°, and that the separation factors of the exchange reactions

$$C_6H_{12} + HD \rightleftarrows C_6H_{11}D + H_2\,, \qquad \text{(VIII)}$$

$$C_6H_6 + HD \rightleftarrows C_6H_5D + H_2\,, \qquad \text{(IX)}$$

differ appreciably, and are equal to 2.3 and 3.0 at 184° and 100° respectively for reaction (VIII) and 1.30–1.35 at 300°–350° for reaction (IX). The process is illustrated in Fig.15. The deuterium is concentrated in the cyclohexane by exchange with hydrogen at 150° in the exchange column *II*. Dehydrogenation at 300° in the dehydrogenation column *III* yields the deuterium-rich hydrogen of the cyclohexane, thanks to the lower separation coefficient of the exchange reaction between hydrogen and benzene.

The benzene can be reconverted to cyclohexane in the hydrogenation column. The operating pressure in the system is 15 atm, and the degree of extraction is fairly high (φ_{max} = 0.48). All the extracted deuterium comes from the hydrogen stream. The difficulty in using this three-component system lies in the lack of a suitable catalyst to ensure hydrogenation and dehydrogenation without the formation of side products. Morever, the level of production is determined by the quantity of hydrogen available.

This review of possible systems for the dual-temperature process shows that the water–hydrogen sulphide and water–hydrogen systems deserve most attention, and more convenient exchange systems are unlikely to be found[62-64]. Some technological and economic data for these two systems are given in Table 9.[35]

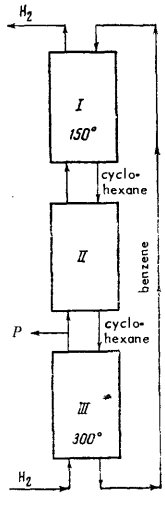


Fig. 15. Dual-temperature exchange in the cyclohexane – hydrogen – benzene system. I) Benzene-hydrogenation column; II) exchange column; III) cyclohexane-dehydrogenation column; *P*) removal of product.

TABLE 9. Comparison of dual-temperature methods for preparing heavy water.

Data	System of deuterium-exchange substances	
	H_2O—H_2S	H_2O—H_2
Temperature, °C	30,120	40,200
Pressure, atm	20	200
Ratio of separation factors	1.24	1.7
Effective degree of extraction	0.16	0.33
Stream ratio	1:2.08	1 : 2.42
Raw material used per kg of D_2O	38 tons of H_2O	26 000 km^3 of H_2
Additional raw material per kg of D_2O	100 000 km^3 of H_2S	8.7 tons of catalyst suspension
Approximate capital expenditure, dollars per kg of D_2O per year	240—285	240—360*
Power consumed per kg of D_2O:		
steam, tons	7	2.1
electrical power, kWh	800	200
Cost of power, dollars per kg of D_2O	36.7	10.5
Approximate cost of 1 kg of D_2O**, dollars	75—80	41—54

* Including 48 dollars per 16 kg of platinum.

** Including 10% depreciation costs, 20% extra charges for operating expenses (wages and salaries), and 10% profit.

TABLE 10. Breakdown of cost of heavy water from Savannah River plant.

Items of expenditure	Dollars per kg of D_2O	% of total operating costs
I. Operating costs		
Feed water	0.88	2.95
Hydrogen sulphide	0.97	3.25
Electrical power	2.93	9.84
Steam	9.71	32.62
Coolant water	0.26	0.87
Maintenance	1.08	3.63
Wages and salaries	5.78	19.42
Various prod. expenses	0.45	1.54
Overhead expenses	7.70	25.87
Total:	29.77	
II. Deductions for capital investmt. at 6% per annum	22.99	
III. Extra charges of the Atomic Energy Commission	8.11	
Cost of heavy water	60.87	

At first sight it might appear that the water-hydrogen system is preferable, but all the calculations are based on the use of hydrogen, purified from catalyst poisons, from plants synthesising ammonia at 200 atm: that is a significant proportion of the cost is related to the synthesis of ammonia. If allowance is made for this, the capital and operating costs for this method are no less than those for the hydrogen sulphide one. Morever, the productivity of the former method, like that of the distillation of hydrogen, is limited by the level of production of hydrogen. According to Weiss this method cannot yield more than 650 tons of heavy water per year.

Table 9 shows that the cost of heavy water from the dual-temperature exchange between water and hydrogen sulphide under European conditions is 75–85 dollars per kg. The cost of heavy water from the American Savannah River plant is 62 dollars per kg. The difference is due to the higher cost of power in Europe. Data on the operating expenses of the Savannah River plant (Table 10) show that the cost of power amounts to more than 40% of the total operating costs. The possibility of reducing the cost of power by using cheap natural sources of steam led the Organisation for European Economic Cooperation to choose a site for the production of heavy water in Hengill (Iceland), where the estimated cost of steam is at most one tenth of that in Western Germany, for example.

When examining the possibilities of the different methods for producing heavy water in large quantities, it should be noted that the dual-temperature exchange between water and liquid hydrogen sulphide is the only method known at present to give a low-cost product in unlimited quantities, and this will undoubtedly become the principal method for the production of heavy water. Hydrogen from nitrogen-fertiliser plants will probably also be used in a number of cases to produce deuterium by the low-temperature distillation of hydrogen, and the isotopic exchange between ammonia and hydrogen may also find some application.

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NUCLEAR MAGNETIC RESONANCE AND THE STRUCTURE OF MATTER

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A diamagnetic substance placed in a static magnetic field and also subjected to an alternating magnetic field of certain frequency will absorb energy from the alternating field. This phenomenon is known as nuclear magnetic resonance because it is due to the nuclear magnetic moments present in the molecules of diamagnetic substances. Nuclear magnetic resonance was first observed

by Bloch[1] and independently by Purcell. Bloch's experiments were based on the fact that a reorientation of the nuclear magnetic moments (related to the angular momentum or spin) gives rise to an induced electromotive force. These experiments are analogous to those of Zavoiski where resonance absorption was observed as a result of a reorientation of the electronic magnetic moments.

Soon after Bloch's experiments it became clear that nuclear magnetic resonance could be used for investigating the structure of matter (e.g. determination of the nuclear magnetic moments, study of molecular and crystal structure, chemical analysis, etc.) Since 1946 this method has developed rapidly; today many hundreds of nuclear magnetic resonance experiments are made and their number grows continuously. It should be pointed out that the discovery and the rapid development of the method were made possible by the progress made in radio-frequency techniques. In this article we shall not deal with problems of technique but we shall try rather to explain the physical principles of nuclear magnetic resonance and indicate certain fundamental applications in the study of the structure of matter.

A nucleus with angular momentum (spin) I possesses also a magnetic moment μ which is parallel or antiparallel[2] to I. The two quantities are related in such a way that $\mu = \gamma I$, where γ is the gyromagnetic ratio of the nucleus (it would be more correct to call γ the magnetogyric ratio since it is the ratio of the magnetic moment and angular momentum of the nucleus). The constant γ, which depends on the nuclear structure, is an important characteristic of the nucleus together with its mass, charge, and angular momentum (spin). For a nucleus which is not subjected to any external forces, the vector I remains unchanged because of the conservation of angular momentum. The situation is different, however, when the nucleus is placed in a static magnetic field H_0, directed along the z-axis, for example. In this case the angular momentum of the nucleus changes; the equation of motion shows that the vector I, though retaining its absolute value, changes direction in space in such a way that it precesses about H_0 with an angular frequency $\omega_0 = \gamma H_0$. This is known as the Larmor precession. The behaviour of vector I can be compared to the precession of a spinning top in the gravitational field.

It is more convenient to explain many physical processes associated with nuclear magnetic resonance in terms of a frame of reference rotating around H_0. We can thus observe the behaviour of the nuclear magnetic moment (which is parallel or antiparallel to I) from the rotating frame of reference. When the angular frequency of its rotation is equal to ω_0, both the magnetic moment and the angular momentum remain stationary as if the external field were absent. Consequently we can say that in the system of coordinates rotating with frequency ω_0 the external magnetic field is zero. However, when the frequency of rotation ω is not equal to ω_0, I and μ perform the Larmor precession with the angular frequency $\omega_e = \omega_0 - \omega = \gamma H'_e$. That is to say, in the rotating system of coordinates there is an effective field $H'_e = H_0 - \omega/\gamma$, which is parallel or antiparallel to H_0.

Let us suppose now that in addition to H_0 we also have an alternating field H_1 which rotates with frequency ω, i.e. the same frequency as that with which the system of coordinates is rotating. In this system H_1 is therefore stationary. Let H_1 be directed along the x-axis of the rotating system. The resultant magnetic field H_e is then obtained by using the vector addition rule as shown in Fig.1.

In the rotating system μ precesses around H_e with Larmor frequency equal to γH_e. Obviously when H_1 rotates with frequency ω_0, then $H'_e = 0$, and $H_e = H_1$. In this case μ precesses around the x-axis (i.e. the H_1 direction) with angular frequency γH_1; for example, if initially μ was along the z-axis then after a time $t = \pi/\gamma H_1$, the vector μ changes its direction by 180°. However if ω is very different from ω_0, that is, $|\omega_0 - \omega| \gg \omega_0 H_1/H_0$, and H_1 is considerably smaller than H_0, then H_e is nearly parallel to H_0 and in the stationary system of coordinates (in which the z-axis coincides with the z-axis of the rotating system) the motion of μ will be very nearly the Larmor precession of μ about the static field H_0, in other words, the motion of the magnetic moment will not be appreciably affected by the presence of H_1.

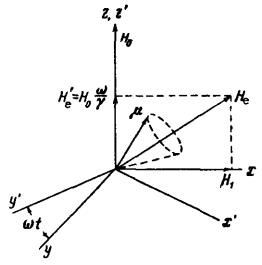


Fig. 1. The magnetic fields in the rotating coordinate system. Coordinates $x\,y\,z$, equal to the frequency of rotation of H_1. H_e is the effective field in the rotating coordinates with $H_1 = 0$. When H_1 is applied, the magnetic-moment vector μ precesses around H_e, (which lies in the xz-plane) with angular frequency $\omega_e = \gamma H_e$.

The mechanism described above forms the basis of nuclear magnetic resonance. Fig.2 represents schematically a typical nuclear-magnetic-resonance experiment.

Sample S containing a large number of magnetic nuclei is placed in a static magnetic field H_0 (H_0 is perpendicular to the plane of the drawing). Since the energy of the magnetic moments in the external magnetic field H_0 depends on their relative orientation, there will be a larger number of

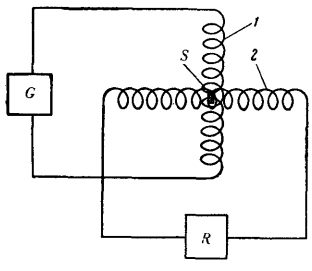


Fig. 2. The principle of a nuclear-magnetic-resonance experiment. G – radio frequency generator ($\omega \sim 10$Mc/s); S – sample; R – receiver used to pick up the induced signals; (1) and (2) are induction coils. The receiver for detection of the absorption signal is not shown in the diagram.

moments aligned along H_0 than in the opposite, energetically unfavourable, direction. This alignment is brought about by the interaction of the magnetic moments and the thermal agitation of the medium (translational and vibrational molecular motion, vibration of the crystal lattice, etc.). In this way the sample becomes polarised and acquires a finite net magnetic moment M_0 directed along the z-axis.

It should be pointed out, however, that complete polarisation is not attained immediately after the application of H_0. The time of polarisation depends on the interaction of the nuclear magnetic moments with the lattice and can be approximately characterised by a quantity T_1, called the longitudinal relaxation time, which determines the time in which the net magnetic moment of the sample reaches its equilibrium value M_0. For typical samples T_1 ranges from a fraction of a second to an hour, e.g. for protons in pure water $T_1 \cong 2$ sec but in LiF T_1 approaches 50 min for Li.

Suppose the sample is subjected to the static field H_0 for a time $t \gg T_1$ so that it becomes completely polarised. Subsequently we switch on the generator G, working at a frequency $\omega_0 = \gamma H_0$ and generating a rotating field H_1 in coil *1* (the term "rotating field" is used in the sense that the field-intensity vector of the alternating field H_1 rotates with respect to the static field H_0)*.

If the generator is applied for a time $t_1 = \pi/2\gamma H_1$, then all the nuclear magnetic moments, initially along the z-axis, will be aligned along the y-axis in the rotating system of coordinates. Consequently the resultant magnetic moment of the sample having the absolute value equal to M_0 will be directed along the y-axis after time t_1, assuming that during this interval there is no appreciable relaxation, i.e. we assume that $t_1 \ll T_1$. For the gyromagnetic ratio of the order of 10^4 oersted^{-1} sec^{-1} and $H_1 \sim 10$ oersted, t_1 must be about 10^{-5} sec, which means that the condition $t_1 \ll T_1$ can be easily satisfied. Moreover, the condition that $H_1 \ll H_0$ is also readily fulfilled since in most nuclear-magnetic-resonance experiments H_1 is about 10 oersted and H_0 is of the order of 10^3 to 10^4 oersted.

When the alternating field is switched off all the nuclear magnetic moments precess about H_0 with angular frequency $\omega_0 = \gamma H_0$, and therefore so does the resultant magnetic moment M (directed along the y-axis of the rotating system of coordinates). The rotating moment M generates an alternating field in coil *2* and induces a voltage across the coil. This voltage is amplified and fed into a receiver R. The signal observed in this way is known as the free-induction signal.

The signal decays in time T_1, because during this interval the sample is repolarised and its magnetic moment is again directed along the z-axis. In fact, the free-induction signal decays in a time shorter than T_1 because the relaxation of the transverse component of M (perpendicular to H_0) is faster than (or equal to) the relaxation of the longitudinal component (parallel to H_0). The physical reasons for this are readily understood. Suppose that H_0 is somewhat inhomogeneous over the sample. We can express the degree of inhomogeneity in terms of $\Delta H = [\overline{(H_0 - \overline{H}_0)^2}]^{\frac{1}{2}}$, where the bar indicates the average taken over the sample. ΔH_0 therefore is the measure of H_0 deviation from the mean value $\overline{H}_0$ (in cases where ΔH is small and the effect of field inhomogeneity in so far as the nuclear moments are subjected to slightly different fields H_0 they will be turned through slightly different angles on application of the alternating field in the experiment described above. These differences will be small and of the order of $\Delta H / H_0$, so that soon after the alternating field is applied, the net magnetic moment of the sample, will have the absolute value approximately equal to M_0 and will point along the y-axis as before. However, when this field is switched off, the nuclear moments situated in slightly different H_0's will precess with somewhat different frequencies. Consequently, even in the absence of the longitudinal relaxation, the transverse component of M decays in a time of the order of $1/\gamma \Delta H$, which is equal to the difference between the extreme Larmor precession periods of the nuclear moments. But even if H_0 is perfectly homogenous, there remains an internal magnetic field due to the nuclear magnetic moments in the sample. This field, which is substantially inhomogeneous, causes relaxation of the transverse component of M without affecting its longitudinal component. On the other hand, the spin–lattice interaction controls the decay of both the longitudinal and the transverse components of M. In this way the decay of the latter is faster, that is to say the transverse relaxation time T_2 is less than T_1.* For example in LiF T_2 is of the order of a few milliseconds, whereas T_1 is many minutes. But in a large number of substances, including gases and the majority of liquids, at room temperature, $T_1 = T_2$. In these substances the local magnetic fields fluctuate very rapidly compared to the Larmor frequency ω_0 (for $H_0 \cong 10^3$ oersted, $\omega_0 \cong 10$ Mc/s), and therefore in one Larmor period a nuclear magnetic moment goes through many different local fields so that on average its precession frequency is not affected. It should be noted that in certain liquids $T_2 \neq T_1$ which indicates a restricted molecular mobility (large viscosity, presence of quasicrystalline structure, formation of molecular complexes, etc.).

The mechanism described above explains these physical processes from the classical point of view only. A more precise description requires quantum mechanics[4,5] which reveals a number of additional relaxation processes without any classical analogues. In spite of the fact that nuclear magnetic relaxation has been extensively studied, there is as yet no complete theoretical treatment of this problem which would allow accurate quantitative analysis of experimental results.

The free-induction experiment discussed above is performed in a time short compared to T_1 or T_2. The spin-echo experiment described below also belongs to the same class[6-8].

* In actual fact an oscillatory field is produced in coil *1*, equal to $2H_1 \cos \omega_0 t$ but this can be represented by two rotating components of amplitude H_1 and angular frequencies ω_0 and $-\omega_0$. One of the components (with frequency $-\omega_0$) does not affect the nuclear-magnetic-moment motion because it is too far away from the resonance condition, i e. $|-\omega_0 - \omega_0| \gg \omega_0 H_1 / H_0$ (see text).

* Since T_1 and T_2 are unequal, the absolute value of the net magnetic moment of the sample may change during the relaxation process. It is therefore necessary to use at least two parameters, T_1 and T_2, to describe the process.

Suppose the sample is placed in a non-uniform magnetic field H_0 such that the decay of the transverse component of M caused by the field inhomogeneity is faster than the decay due to the internal relaxation processes. After the vector M is turned through 90° by the alternating field the individual nuclear magnetic moments precess with slightly different frequencies because of H_0 inhomogeneity. At a time τ ($\tau \ll T_1$ or T_2) when the free-induction signal has decayed completely, we again apply the alternating field which rotates each nuclear magnetic moment around the x-axis of the rotating system of coordinates. By adjusting the time during which this field is applied it is possible to reverse the phases of the precessing nuclear moments. Since the frequencies of precession remain unchanged by this procedure, all the nuclear magnetic moments will again be aligned at a time τ after the second pulse in the same way as they were after the first pulse. This will lead to a free-induction signal induced in coil *2*. The shape of the signal depends on the H_0 distribution over the sample. This signal is known as the spin echo. We can use the following simple analogy to illustrate this phenomenon.

Let us suppose that a group of runners has started simultaneously from the starting line (the first pulse). Though all the runners were initially in one line, after some time has elapsed, they will spread along the track because of the differences in their individual speeds (the decay of the free-induction signal). At a time τ all the runners turn back and continue to run at their previous speeds (the second pulse). It is quite clear that at a time τ later they will reach the starting line simultaneously (the spin-echo signal). Using this model, we can also show how the field inhomogeneity governing the Larmor frequency distribution determines the shape of the signal. If our runners have very different speeds then they will be grouped together only just before they reach the starting line on their return (narrow signal); on the other hand if they have very similar speeds they will bunch together even a long way from the starting line (broad signal).

Another class of nuclear-magnetic-resonance experiments makes use of nuclear magnetic absorption. These experiments are performed in a time long compared to T_1 or T_2. The alternating field is applied continuously and not in pulses so that the nuclear magnetic moments continuously precess around the H_1 direction (in the rotating system of coordinates). The relaxation processes tend to repolarise the sample and restore the equilibrium (disturbed by the alternating field) between the spin system and the thermal agitation of the medium. There is then a net transfer of energy from the alternating field to the thermal motion of the medium via the nuclear magnetic moments; in other words, the sample is heated. Naturally the heating effect is very small because at normal temperatures the energy of thermal motion is considerably higher than the interaction between the nuclear spins and H_0. Nevertheless, it is possible with the aid of modern amplifiers to detect this absorption of energy occurring in coil *1*, when the resonance condition ($\omega = \omega_0$) is satisfied. We can obtain a spectrum of the nuclear absorption (or induction if we observe the signal in coil *2*) by varying the frequency of the generator or by changing the magnitude of H_0. We can in this way measure the differences between the nuclear-magnetic-moment energy levels. In principle, this phenomenon is identical with optical absorption (or emission)

We shall now discuss some of the basic applications of nuclear magnetic resonance.

In the first place, since $\omega_0 = \gamma H_0$, we can determine the nuclear gyromagnetic ratio by measuring ω_0 and H_0. The magnetic field cannot as yet be measured very accurately, but the resonant frequency can be determined with great precision. This means that the accuracy achieved in absolute measurements of the gyromagnetic ratio is limited by the degree of precision with which the magnetic field is determined. It should be possible to make relative measurements of γ as accurately as the determination of frequency. Unfortunately any non-uniformity of H_0 broadens the magnetic-resonance absorption line (nuclei subjected to slightly different H_0 display absorption at slightly different frequencies). This limits the resolving power of the apparatus. The accuracy is further limited by any instability of H_0. The manufacture of high-stability magnets producing very homogeneous fields presents a complex technical problem. Nevertheless, the nuclear-magnetic-resonance spectrometers now available have resolving powers of up to 10^8, i.e. it is possible to resolve two resonance lines separated by a fraction of a cycle while their resonant frequencies are of the order of 10 Mc/s.

The resonant frequency of a given nucleus depends on the molecule which contains the nucleus and on its position in the molecule. This displacement of the resonant frequency depending on the molecular structure is known as the chemical shift. The shift is due to the fact that each nucleus is surrounded by an electron cloud which under the influence of the external field H_0 produces a diamagnetic moment giving rise in turn to a magnetic field $-H'$ at the site of the nucleus. H' is proportional to H_0, i.e. $H' = -\sigma H_0$. One could say that the nucleus is magnetically screened and that in fact it is subjected to a field $H_0' = (1 - \sigma)H_0$ instead of H_0. The magnetic screening constant σ, and consequently the effective static field H_0' and the resonant frequency, depend on the molecule and on the position of the nucleus in the molecule. The chemical-shift studies are therefore of particular interest from the point of view of physical chemistry and molecular physics[9]. We shall now give a few examples.

First of all, the chemical shift can be used as an analytical tool in a way analogous to optical-spectrum analysis, i.e. by making a systematic classification of the magnetic-resonance lines associated with specific molecules and atomic groups we can subsequently establish the presence of a certain atomic group in the sample from the presence of these lines in its spectrum, and from their intensity we can determine the concentration of the group. So far this method has not been much developed and its accuracy is inferior to other analytical procedures, but it has the great advantage that it affects neither the chemical composition of the sample nor its molecular motion, which cannot be said, for example, of the emission spectrum analysis.

Secondly, nuclear-magnetic-resonance spectroscopy can be used to determine various isomeric molecular structures. As an illustration of the method let us consider the nuclear-magnetic-resonance spectrum of ethyl alcohol, C_2H_6O (Fig.3). The spectrum consists of three lines corresponding to the three non-equivalent proton positions. Furthermore, since the areas under these lines (i.e. their integral intensities) are in the ratio 3 : 2 : 1, we conclude that the number of protons in the first, second, and third non-equivalent positions is in the same ratio. Finally, knowing that the total number of protons in the molecule is 6, we arrive at the following structure: CH_3-CH_2-OH. In this case, of course, the molecular structure could be easily obtained without the aid of nuclear magnetic resonance but in more complicated molecules the method is extremely valuable.

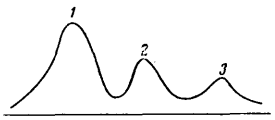


Fig. 3. Nuclear-magnetic-resonance spectrum in liquid ethyl alcohol showing the chemical shift. Lines *1*, *2*, and *3* correspond to the protons in CH_3, CH_2, and OH groups respectively.

Finally, the chemical shift contains information about the electronic-cloud structure. But before we can use the available data on chemical shift, we must have theoretical estimates of the screening constants. There are many papers on this subject, but because of the great mathematical difficulties involved any accurate calculation of the screening constants is apparently impossible without the aid of an electronic computer.

In addition to showing a chemical shift, nuclear-magnetic-resonance lines, are often split, owing to the intramolecular interaction between nuclear magnetic moments. As pointed out above, the magnetic interaction between neighbouring nuclei gives rise to the relaxation phenomena. This interaction broadens the resonance line, but it does not produce any splitting since its magnitude depends on the orientation of the molecule with respect to the external static field H_0. The line splitting is due to the fact that the nuclear magnetic moment polarises the electronic cloud of the molecule, which in turn creates an additional magnetic field at the neighbouring nucleus. This effect does not depend on the external field H_0. The magnitude of the splitting associated with this "indirect coupling" is, like the magnetic screening constant, dependent on the electronic-cloud configuration in the molecule; it therefore provides yet another method for studying molecular structure. Examples of such spectra and detailed lists of many papers on magnetic resonance may be found in the literature[10-12].

In crystals the transverse relaxation time T_2 is considerably shorter than in liquids. The presence of non-uniform local magnetic fields results in a very broad line (by comparison with liquids), whose shape reflects the local-field distribution. If the local-field inhomogeneity is determined solely by the adjacent magnetic nuclei, then it is possible to establish their configuration in the lattice. Several crystals have been examined in this way and proton positions determined with precision comparable to the neutron scattering method; protons are not easily located by X-ray.

Any rapid motion in the sample averages out local-field inhomogeneities and the resonance line becomes narrow. This phenomenon is found in crystals when certain atomic groups begin to rotate. We can thus investigate the nature of the internal motions of a crystal by observing its line width as a function of temperature.

Let us finally consider an interesting effect connected with chemical exchange in liquids[13]. If in a liquid there is a chemical equilibrium $AH \rightleftharpoons HB$, then the proton-exchange frequency between the A and B groups governs the shape of the proton-resonance line. When the exchange frequency is sufficiently low (in the limiting case there is no exchange of protons), the protons contained in the AH group have a resonant frequency ω_{pA} and those in the HB group resonate at ω_{pB} ($\omega_{pA} \neq \omega_{pB}$ because of the chemical shift). The situation is changed when the proton-exchange frequency is greater than $\omega_{pA} - \omega_{pB}$. We can easily see the effect by considering the motion of a proton magnetic moment from the point of view of an observer situated in a frame of reference rotating with frequency $\frac{1}{2}(\omega_{pA} + \omega_{pB})$. When the proton is in molecule AH, its magnetic moment, in the rotating system of coordinates, precesses with frequency $\frac{1}{2}(\omega_{pA} - \omega_{pB})$, but when it is contained in the HB group the proton precesses with the same frequency but in the opposite direction. Therefore, when the rate of exchange is much faster than the proton-precession frequency, in the rotating system of coordinates the proton remains stationary. Consequently, there will be only one resonance line in the spectrum corresponding to the frequency equal to $\frac{1}{2}(\omega_{pA} + \omega_{pB})$.

If the rate of exchange is equal to $(\omega_{pA} - \omega_{pB})$, then the line will have some intermediate form which, if known, will enable us to determine the proton-exchange frequency.

Soon after nuclear magnetic resonance was discovered, it was applied to the study of crystalline and amorphous polymers. Powles[14], for example, has shown that in amorphous polyisobutylene (repeating unit $-(CH_3)_2-CH_2-$) the distance between the hydrogen atoms belonging to the CH_3 groups in neighbouring repeating units can be less than twice the hydrogen van der Waals radius. Later, it became evident that the regularity of the side-chain configuration influences the line width and this fact makes it possible to study this important property of polymers.

Most of the nuclear-magnetic-resonance experiments in polymers are devoted to the study of their thermal motions (see the detailed review by Slichter[15]). The line width is reduced and T_1 and T_2 are altered by these motions, and therefore by measuring these quantities as a function of temperature we can obtain information about the nature of the motion and of transitions between solid and liquid phases, such as crystallisation and glass formation. The results obtained from such nuclear-magnetic-resonance measurements turn out to be in general agreement with dielectric and mechanical data. Nuclear magnetic resonance thus supplements other methods used in the investigation of molecular movements, but, unlike the dielectric method, it can be applied to substances devoid of polar groups. Also, the application of the magnetic field to the sample has no effect on the molecular motion; this cannot be said of either the mechanical or the dielectric method.

Study of the dependence of T_1 and T_2 for polymers on temperature and frequency[16,17] reveals very complex molecular motions in polymers. In particular, on raising the temperature of molten polymers, T_1 and T_2 do not approach each other, as they do in liquids of small molecular weight (see above).

The so-called crystalline polymers are not completely crystalline because they contain a certain amount of the amorphous phase. At temperatures above the glass transition temperature, and below the melting point, the amorphous part is in a fluid state and gives rise to a narrow resonance line, whereas the crystalline part has a broad line. The resulting compound line is a combination of a narrow line superimposed on a broad one. In a num-

ber of cases it is possible to separate the narrow and the broad lines and determine the degree of crystallinity from the areas under these lines. Unfortunately this method for determining the degree of crystallinity has a very limited application, because it is not always possible to separate the two lines.

Resonance lines composed of a narrow and a broad line are also observed in polymers containing low-molecular--weight components which move much more rapidly than the molecule of the polymer[18]. In the process of polymerisation by cross-linking the molecular movements change; this makes it feasible to study polymerisation kinetics by nuclear magnetic resonance. We have to remember, however, that the line width and the relaxation times refer to the entire polymer only if it has a comparatively low molecular weight. For polymers with long molecules, the line width is not determined by the motion of the molecule as a whole but by the motion of its segments with independent orientations.

In view of the high viscosity of polymer melts, their chemical shifts and nuclear-magnetic-resonance spectra can be obtained only in solutions. Some experiments of type, showing good resolution of lines in magnetic--resonance spectra of polymer solutions, have recently (1959) been reported in literature[19,20].

In conclusion let us consider briefly the recently developed electron and nuclear double-resonance method. This method is employed for studies of paramagnetic samples, i.e. samples containing an appreciable number of unpaired electrons (and consequently, an appreciable number of electronic magnetic moments, which are about 10^3 times larger than the nuclear moments). Obviously, the local magnetic fields are extremely large so that the nuclear--resonance line becomes too broad to be observed. On the other hand, the electron-paramagnetic-resonance lines[21] are so broad that it is also impossible to distinguish the components corresponding to the energy levels of individual nuclei. Therefore in order to obtain information about the energy levels of the nuclear spins, we can try to act simultaneously on the electronic and the nuclear moments by means of an alternating magnetic field. This is exactly what is done in a double-resonance experiment. That is to say, the principle of the double-resonance experiment is to apply an additional alternating field at a frequency corresponding to the nuclear resonance while the electron resonance is being observed (i.e. absorption of energy by the electronic magnetic moments from the alternating field). The interaction between the nuclear and electronic magnetic moments results in a modification of the electron-resonance signal which can be detected experimentally. Consequently, by varying the frequency of the alternating field in the region of the nuclear Larmor precession frequency we can determine certain nuclear resonant frequencies of interest, using the electron-resonance signal as an indicator. In so far as the effect under investigation is governed by the interaction between the nuclear and electronic magnetic moments, it is also possible to reveal in this way the nature of the electronic motion in the sample. Feher has made such experiments, which enabled him to determine with great precision the electron-density distribution in a paramagnetic crystal.

We have collected here only a few applications of nuclear magnetic resonance to the study of the structure of matter. Nevertheless, even from the examples described above, it is apparent that this method has great possibilities. There is little doubt that the nuclear-magnetic-resonance spectrometer will become as familar in our laboratories as the ordinary optical spectrometer is now.

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THE MAIN LINES OF RESEARCH ON THE CHEMICAL REACTIONS OF MACROMOLECULES

A. A. Berlin

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INTRODUCTION

The development of synthetic chemistry has led to the production of an immense variety of polymeric substances, differing in chemical and spatial structure. As experimental knowledge of the conversion of monomers into high polymers has accumulated, investigators have been faced with the ever more urgent problem of studying the effect of various chemical, physical, and mechanical factors on the structure and chemical reactions of macromolecules. Work on these lines has been stimulated by the requirements of industry, which has been interested in modifying the properties of polymers and in obtaining comprehensive information about their operating characteristics. Solution of the problems of modifying the properties of polymers made it necessary to develop methods of carrying out chemical changes in macromolecules in order to obtain materials having specified properties.

The search for methods of modifying the properties of polymers has led, especially during the past 10–15 years, to new synthetic processes for converting one class of polymer into another, for introducing different atoms and groups into macromolecules, "hybridising" macromolecules by chemical grafting and linking together different blocks, and producing marked changes in the properties of polymers by intramolecular cyclisation, partial degradation, and the introduction of appropriate atoms and groups.

The voluminous experimental results which have accumulated on the chemical reactions of macromolecules[1] call for a rational classification which will facilitate systematisation and also the planning of new methods for modifying the properties of polymers. It is convenient to base this classification on the process producing the change in composition, struc-

ture, and properties of the macromolecules. In this way the whole range of reactions in which polymers participate can be combined into four main groups:

I. Intramolecular reactions in macromolecules.

II. Reactions of atoms, functional groups, and active centres in macromolecules unaccompanied by growth of the polymer chains.

III. Chain growth due to interaction between terminal atoms, groups, and active centres* of the macromolecules (block copolymerisation).

IV. Chain growth due to chemical reactions of groups and active centres within the macromolecules.

Group I includes dehydrogenation, dehydrochlorination, dehydration, and other elimination processes, as well as intramolecular cyclisation. As a result of these reactions, the structure and configuration of the main chain are changed without appreciable change in the degree of polymerisation.

Group II incorporates the chemical reactions of macromolecules which involve reactive atoms and functional groups of the main chain and substances of low molecular weight. Among them must be included addition reactions to double bonds in macromolecules (hydrochlorination, halogenation, hydrogenation, hydration, etc.), substitution reactions of atoms in the main chains or side groups of macromolecules (sulphonation, halogenation, alkylation, chloromethylation, etc.), and numerous chemical reactions of functional and other reactive groups.

Group III includes reactions between terminal groups or active centres of polymer molecules and monomeric or polymeric substances leading to the formation of high-polymer chains consisting of repeating sections or blocks having a definite size, composition, and structure.

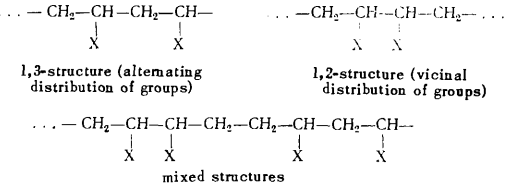
Group IV comprises reactions between polymers containing active centres along the chain with polymerisable monomers or reactive polymers.

In such processes branched or three-dimensional compounds of high molecular weight are formed, known as graft copolymers. This group includes also the "cross-linking" reactions, involving active centres, double bonds, and functional groups of the macromolecules. The suggested classification is to a considerable extent arbitrary, since many chemical reactions of polymers occur by a complex mechanism involving processes of different types at the individual stages.

Chemical changes in macromolecules may occur both by molecular and by ionic or radical mechanism. The magnitude of the activation energy necessary for reactions of different functional groups and atoms in polymer chains is practically the same as that required for the same reactions to occur with monomeric substances similar in structure to the units in the polymer chain[1]. Nevertheless, in most cases functional groups and the macromolecules themselves react considerably more slowly than do analogous substances of low molecular weight. This is explained by the fact that reactions involving polymer chains are more complicated, since the reaction velocity is affected by intermolecular forces, the shape and flexibility of the macromolecules, and other factors affecting the pre-exponential term in the Arrhenius equation.

* Active centres in macromolecules are atoms having electrons with unpaired spins or groups which can form free radicals.

The polymerisation of unsaturated monomers leads to the formation of isomers in which different arrangements of functional groups are theoretically possible:



Determination of the factors that influence the formation of a particular structure in the polymer chain is of fundamental importance in elucidating the relation between the structure and the reactivity of macromolecules. In order to understand this as yet unstudied question it must be remembered that mutual repulsion forces must be overcome in order to form 1, 2-structures, involving greater consumption of energy than the formation of 1,3-structures.

Hence it follows that raising the temperature of polymerisation must affect not only the mean degree of polymerisation but also the structural isomerism of the high polymers. Harsher conditions of polymerisation increase the probability of the vicinal distribution of substituents, which must increase the internal energy and the reactivity of the polymer.

Available experimental data support these theoretical ideas. Thus it has recently been shown that the relative proportions of 1,2- and 1,3-structures in polyvinyl alcohol and polyvinyl chloride) depend on the conditions of polymerisation, and that the presence of even a comparatively small amount of the 1,2-structures exerts a great influence on the chemical properties of compounds of high molecular weight[1]. Investigation of the structure of polyvinyl alcohol prepared by saponification of polyvinyl acetate synthesised at 35° and 50° showed that the ratio of 1,2- and 1,3-structures in the former product did not exceed 1 : 110, whereas in the latter case it reaches 1 : 50. Polyvinyl alcohol enriched with the vicinal structure contains the 1,2-glycol group and readily undergoes oxidative degradation under the influence of air or HIO_4.

Vicinal polyvinyl chloride synthesised by chlorination of polybuta-1,4-diene is characterised by diminished thermal stability, splitting off HCl to form an insoluble product on slight heating or even on repeated dissolution[2]. Partly dehydrochlorinated polydichlorobutadiene contains isolated and conjugated double bonds.

The reactivity of macromolecules and the types of chemical changes they undergo should be influenced by stereoisomerism as well as by structural isomerism. Unfortunately, this important question still remains uninvestigated, although it has no less scientific and practical interest than the investigation of the physical and mechanical properties of stereoregular polymers.

I. INTRAMOLECULAR REACTIONS IN MACROMOLECULES

Intramolecular reactions occur in polymer chains by the elimination of reactive atoms and groups or by intramolecular cyclisation under the influence of heat, light, or radiation, as well as by the action of acids, bases, complex-forming salts, and some other reagents.

1. Intramolecular Elimination Reactions

Intramolecular elimination has great scientific and practical interest, since such reactions can be used to prepare polymers having a system of conjugated double bonds (polyvinylenes). These polymers should exhibit the features of the so-called "metallic covalent" bond[2], which endows the polymer with high thermal stability, increased electrical conductivity and magnetic properties[2-6].

A soluble polyvinylene is most readily obtained by eliminating HBr from polyvinyl bromide by the action of alcoholic alkali or organic bases[5]. A similar change may also be brought about by the thermal dehydration of polyvinyl alcohol. The conversion of polyvinyl bromide and polyvinyl alcohol into polyvinylenes is achieved by thermal or chemical treatment of these polymers in the form of fibres and films. The dark brownish polyvinylenes formed by these reactions possess well defined dichroism and semiconductor properties in the oriented state; the electrical resistivity of films of these materials is diminished by a factor of ten on heating to 60°–70°.[5]

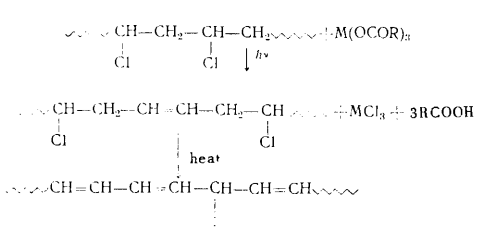
Work was carried out not long ago on the conversion of polyvinylidene chloride, and its copolymers into polyvinylenes[6]. Elimination of HCl was achieved by boiling with morpholine or heating with alcoholic alkali in nitrogen under reduced pressure. Such treatment yielded insoluble dark-coloured polymers containing 7.3–17.5% of combined chlorine and having a magnetic susceptibility of $+1.56 \times 10^6$, wich corresponds to a magnetic moment of 1.19 Bohr magnetons or one free electron for every 18 carbon atoms along the conjugated chain. Analysis for the elements and infra-red spectroscopy indicated the presence of CH_2 and CCl_2 groups, which suggested that conjugation had broken down in some sections of the chains. The dependence of electrical resistivity on temperature for the product of the dehydrochlorination of polyvinylidene chloride is shown in Fig.1, from which it is seen that these substances exhibit semiconductor properties, evidently due to delocalisation of π electrons in the conjugated chain.

Halogenated polymers may also be converted into brownish polyvinylenes by ultra-violet irradiation[7].

The formation of chromophoric polyene groups on irradiating polyvinyl or polyvinylidene chloride is markedly accelerated by the introduction of Al or Fe stearate into the polymer. The catalytic action of these salts is explained by the fact that the HCl which is split off under the action of light reacts with Al and Fe to form the corresponding halides, which are active dehydrochlorination catalysts.

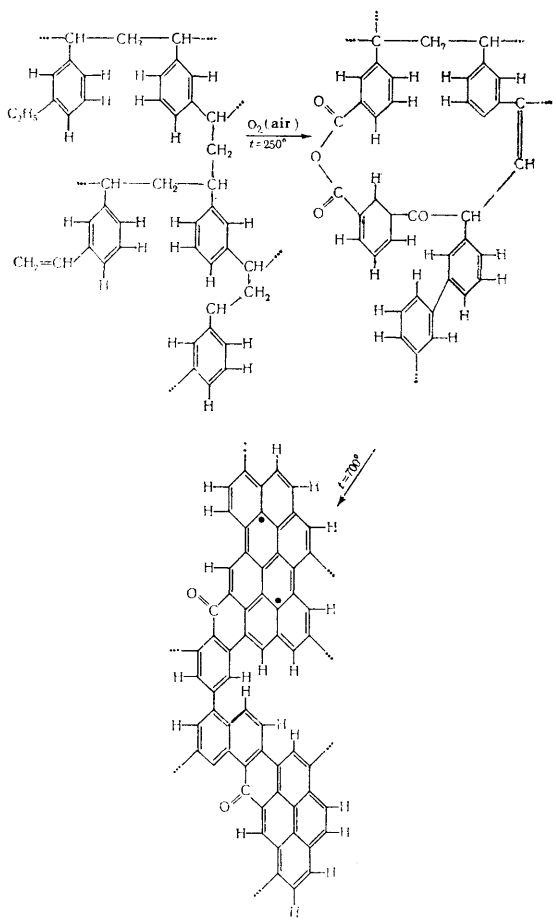
The ability of halogenated polymers to form coloured dehydrochlorination products has been successfully used to prepare light-sensitive plastics and coatings, enabling a photographic image to be obtained directly on the surface of articles[8].

The chemistry of photography on plastics can be represented by the following scheme:



When polyvinyl chloride containing Al or Fe stearate is irradiated with visible light, the bonds which are unstable to this type of radiation are weakened, leading to the elimination of HCl and the formation of Fe^{3+} or Al^{3+} chloride. Increasing the intensity of the radiation accelerates the dehydrochlorination, and thus increases the formation of chlorides which catalyses this process. Subsequent heating of the irradiated material leads to rapid dehydrochlorination, formation of chromophoric groups, and the development of colour.

Aromatisation processes occurring during the pyrolysis of certain three-dimensional polymers are of considerable theoretical and practical interest. Condensed aromatic systems were obtained in the pyrolysis of poly-*m*-divinylbenzene and of copolymers of *m*-divinylbenzene with *m*-ethylstyrene[9]:



The maximum increase in electrical conductivity is achieved in the pyrolysis of the polymer of *m*-divinylbenzene at 600°–700°, in which polyaromatic compounds containing a system of conjugated bonds[9] are formed (see Fig.2).

An extremely interesting intramolecular reaction occurs on prolonged heating of polyacrylonitrile at 200° (up to 500°). When polyacrylonitrile fibre is exposed to a temperature of 200° for many hours, the fabric becomes black and lustrous, and the polymer loses its solubility. Cloth treated in this way becomes more brittle and less strong, but is nevertheless suitable for certain practical applica-

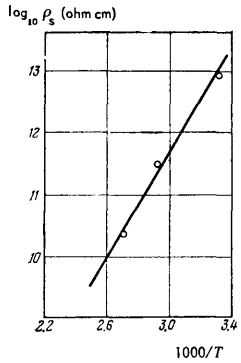


Fig. 1. Dependence of electrical resistivity on temperature for the product of the dehydrochlorination of polyvinylidene chloride.

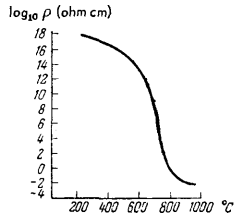
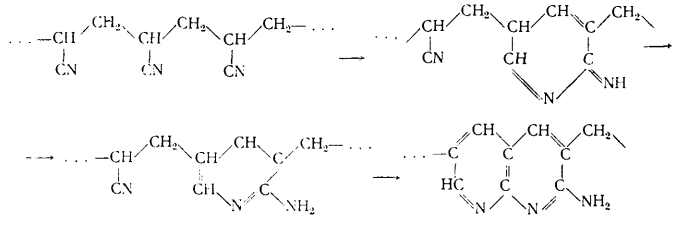


Fig. 2. Electrical resistivity of the product of oxidative pyrolysis of poly-*m*-divinylbenzene as a function of the temperature of pyrolysis.

tions. It is curious that such cloth is not damaged by a Bunsen flame, and can be used at 300°–400°.[10]

It is suggested that polyacrylonitrile undergoes oxidative dehydrogenation and intramolecular cyclisation during heating, leading to the production of polymers having a system of conjugated bonds[10]:



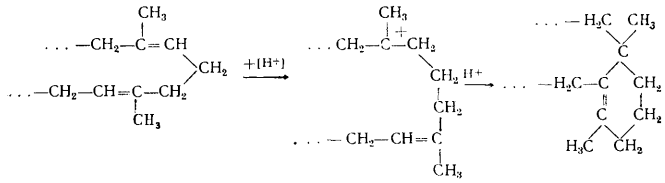
Products of the heat treatment of polyacrylonitrile contain unpaired delocalised electrons[11]. The electrical conductivity of such polymers rises sharply with rise in temperature above 300°. In this respect, products of the oxidative thermal degradation of polyacrylonitrile behave in an analogous manner to polyphenylenes[12] and polyarylvinylenes[12–14] as well as to the types of polymers with conjugated bonds described above.

Thus the development of systematic methods for converting saturated polymers into polyvinylenes or aromatic compounds opens up new possibilities for modifying the properties of polymers, especially for increasing their thermal stability, electrical conductivity, optical and electrical anisotropy, and some other special properties.

2. Intramolecular Cyclisation

This occurs when a macromolecule contains reactive groups situated at distances which are suitable for the formation of five- or six-membered rings when they react. Since cyclic structures are formed in such processes, the rigidity of the macromolecules is markedly increased, which entails a rise in the vitrification temperature and in the viscosity of the polymer. In several cases, intramolecular cyclisation enables the adhesive properties to be improved and other new properties to be conferred on the material.

An example of intramolecular cyclisation is the production of the so-called "cyclised rubber". When natural rubber is slowly heated or is treated with sulphuric acid, sulphonic acids, sulphuryl chloride, or hexachlorostannic acid, it is converted into a hard, brittle product, which is used in the production of adhesives and protective coatings[15]:

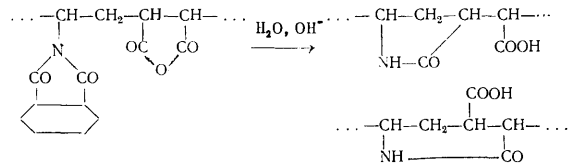


If a macromolecule contains hydroxyl and carboxyl groups, intramolecular lactonisation is possible. Thus the action of an alcoholic solution of a mineral acid on the copolymer of maleic anhydride and vinyl acetate leads to the formation of γ- and δ-lactones[16].

Increase in the rigidity of the chains due to intramolecular lactonisation entails an increase in the ultimate tensile strength and a decrease in the extension at break.

The formation of lactam rings in various polymers was achieved quite recently. Intramolecular lactamisation is possible with polymers containing NH_2 and COOH groups, or groups from which these are readily formed[17].

The simplest example of this type of change is the reaction of the copolymer of vinylphthalimide and maleic anhydride with aqueous solutions of quaternary ammonium bases:



The recently developed intramolecular lactamisation based on the use of the classical Curtius reaction is also of interest[18]. When this reaction is carried out, a large number of butyrolactam units are formed, but complete conversion is not observed and more than 10% of unchanged carboxyl or isocyano groups remain.

Lactamised polymers are beginning to attract the attention of technologists, since they resemble polymers of vinylpyrrolidone (vinylbutyrolactam)[19] in properties, and consequently may find application in medicine (as a substitute for

blood plasma) and in industry (textile finishes, thickeners, emulsifiers). Opening up the lactam rings yields polymers containing both acidic and basic groups, which find application as ion-exchange resins.

II. REACTIONS OF MACROMOLECULES WITH SUBSTANCES OF LOW MOLECULAR WEIGHT UNACCOMPANIED BY CHAIN GROWTH

Among the great variety of reactions of macromolecules which occur without substantial increase in length of the main (or side) chain, we shall confine ourselves to those which have been developed or have acquired importance during the past 8–10 years.

1. Substitution Reactions

An extremely promising method of modifying polymers is chlorosulphonation. Introduction of SO_2Cl groups into polyethylene and several other polymeric olefines yields various products which can be vulcanised to form thermally stable, strong, and chemically resistant polymeric materials[20]. Polyethylene can be chlorosulphonated by reaction of the polymer (M_{av} 20 000) with SO_2 and Cl_2. The main process is accompanied by chlorination of the polyethylene, as a result of which the product contains 1.3–1.75% of sulphur combined as SO_2Cl groups and 26–29% of chlorine.

Infra-red spectroscopy and chemical analysis of chlorosulphonylpolyethylene show that one chlorosulphonyl group is present for every 90 carbon atoms, and one Cl atom for every 7 carbon atoms.

The presence of SO_2Cl groups makes chlorosulphonylpolyethylene capable of numerous reactions, which are used to obtain various sulphonyl derivatives and vulcanisates[21]. Thus when alkylamines (e.g. butylamine) act on a 10% solution of chlorosulphonylpolyethylene in toluene at 25° for 24 h, a sulphonamide derivative is formed:

$$RSO_2Cl + 2R'NH_2 \rightarrow RSO_2NHR' + R'NH_2 \cdot HCl.$$

When this reaction is carried out in more concentrated solutions, the mass is observed to gel, owing to intermolecular association between the sulphamoyl groups. The resulting gel is soluble in toluene and butylamine.

Chlorosulphonylpolyethylene reacts with oxides of bi- and multi-valent metals in the presence of traces of water at 25°–150°, forming salt cross-links[22] to yield insoluble, thermally stable products:

$$RSO_2Cl + H_2O \rightarrow RSO_3H + HCl\ ,$$

$$2RSO_3H + PbO \rightarrow RSO_2OPbOSO_2R.$$

Similar reactions occur when the dry polymer interacts with organic di- and poly-amines at room temperature or above[23].

At elevated temperatures amide derivatives of chlorosulphonylpolyethylene react vigorously with isocyanates, aldehydes, and also with chlorosulphonylpolyethylene itself[21].

$$2RSO_2NHR' + R''(NCO)_2 \rightarrow (RSO_2NR'CONH)_2R'',$$

$$2RSO_2NHR' + CH_2O \rightarrow (RSO_2NR')_2CH_2 + H_2O\ ,$$

$$RSO_2Cl + RSO_2NHR' + MO \rightarrow RSO_2NR'SO_2R + M(OH)Cl.$$

Chlorosulphonylpolyethylene can be vulcanised by means of melamine, salts of multivalent metals, the usual accelerators (mercaptobenzothiazole, thiuram, etc.), quinones, and benzidine. However, these aromatic compounds can react with SO_2Cl groups only at comparatively high temperatures (125°–150°).

Chlorosulphonated polyethylene ("Hypalon") is soluble in aromatic and chlorinated hydrocarbons. Vulcanised Hypalon (containing 40 g of PbO or 20 g of MgO per 100 g of polymer) is very stable to oxidising agents (e.g. ozone), and are chemically stable to light and the atmosphere. The ultimate tensile strength of such compositions without a filler reaches 240–250 kg cm^{-2} at an extension of 200–600%. Heating Hypalon at 190°–200° for 5–10 h reduces the tensile strength to 100 kg cm^{-2}*. At 170° this decrease in strength is reached only after heat treatment for 10 days, and on heating to 120° after almost three months. These results show that Hypalon surpasses rubbers of many types in strength and heat resistance.

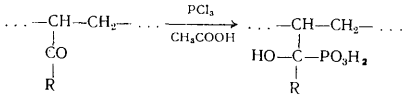
The electrical insulating properties of Hypalon are intermediate between those of natural rubber and Neoprene. Hypalon insulation can be successfully employed at temperatures up to 125°.

Vulcanised chlorosulphonated polyethylene is finding increasing application for the lining of chemical equipment, the manufacture of chemically and thermally stable packing, the electrical insulation of leads for low and medium voltages, and as floor-covering materials. Hypolon varnish coats are transparent and elastic, and possess good adhesion to metals, rubber, wood, and plastics[22,23].

Chlorosulphonation may be employed to modify the properties of polystyrene, polybutadiene, and stereoregular polymeric olefines.

2. Reactions of Functional Groups in Macromolecules

Recently developed methods for the phosphorylation of polymers are interesting, from both theoretical and practical aspects. For example, a mixture of phosphorus trichloride and glacial acetic acid acts on carbonyl-containing polymers in dioxan at 20°–25° to convert the carbonyl groups into hydroxy-phosphonic groups[24]:



Investigation of this reaction with poly(alkyl vinyl ketones) and copolymers of alkyl vinyl ketones with α,β-unsaturated aldehydes showed that increase in the size of the radical greatly increases the difficulty of reaction between the phosphorus trichloride and the keto groups of the polymer. The best results were obtained in the phosphorylation of polymers of methyl vinyl ketone and acrolein, as well as their copolymers with styrene and acrylonitrile.

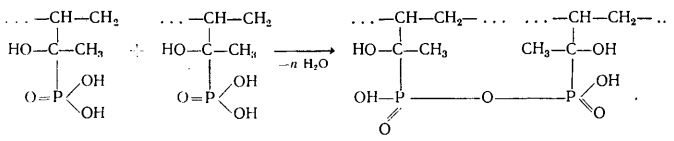
Several halogenated derivatives of tervalent phosphorus are also able to add on to the keto groups of a polymer, the best results being obtained with phenoxydicholorophosphine.

Copolymers containing hydroxy-phosphonic acid groups are readily converted on heating into infusible, insoluble

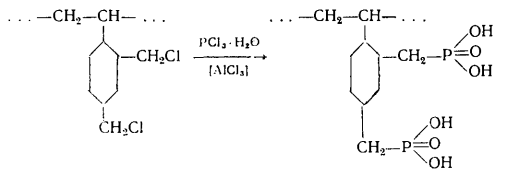
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* The original Russian has "reduces the extension at fracture to 100 kg cm^{-2}". The intended meaning may be "reduces the extension at fracture to 100%" (Ed. of Translation).

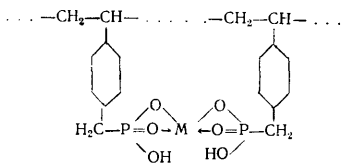
products:



In addition to the phosphorylation of polymeric ketones and aldehydes, methods of introducing hydroxy-phosphonic groups into chloromethylated polystyrene and copolymers of chloromethylstyrene with divinylbenzene, methyl methacrylate, and several other monomers[24] are also of interest. Reaction of these polymers with PCl_3 in the presence of $AlCl_3$ with subsequent oxidative hydrolysis yields the corresponding polymeric phosphonic acids:



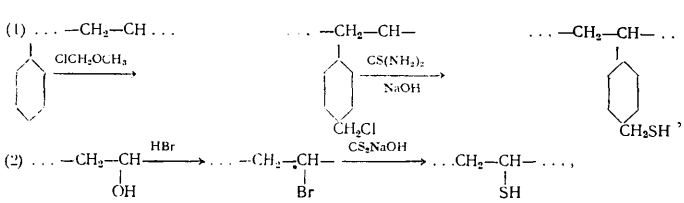
Polyvinyl chloride and phenol-formaldehyde resins have been phosphorylated by analogous methods. Phosphorylation enables the material to be made non-flammable. Further, the presence of phosphonic groups in a polymer makes it able to form chelate complexes with ions of transition metals (Fe^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}, etc.)[25,26]:

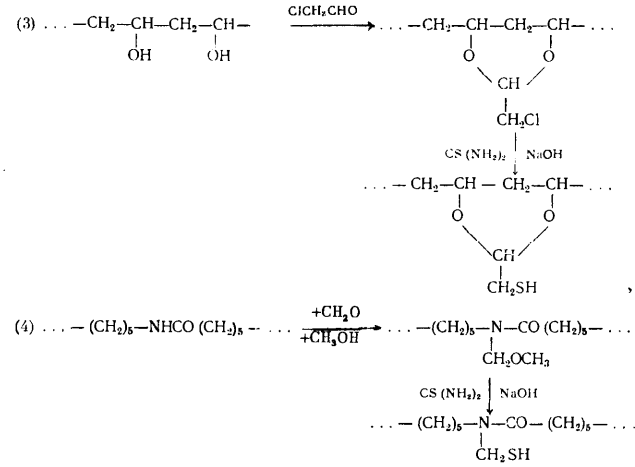


Phosphorylated copolymers of 2,4-bis(chloromethyl)-styrene are therefore used as selective adsorbents for ions. The possibility of cross-linking phosphorylated polymers by forming intermolecular chelate rings can be successfully employed to produce thermosetting plastics[26]. These materials may be expected to combine great strength and heat-resistance with an interesting set of physical properties.

Some recent papers deal with methods of introducing mercapto groups into macromolecules. The synthesis of polymeric thiols is of considerable interest, since thiols readily take part in oxidation-reduction processes and are able to initiate and control many radical-chain reactions. It is these properties of thiols which are responsible for their important role in biological processes.

Mercapto groups can be introduced into polymers by the following reactions[27]:

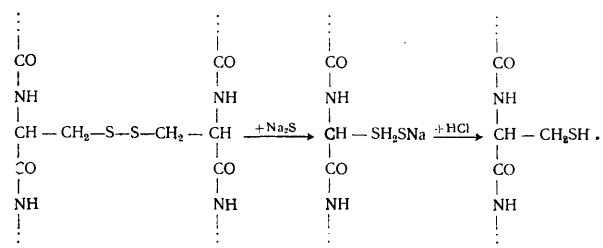




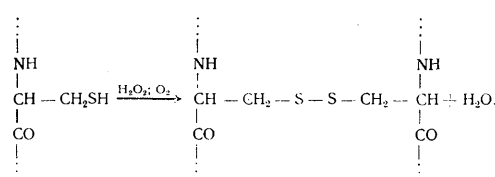
Polymeric thiols, in contrast to those of low molecular weight, have almost no unpleasant odour. They are readily oxidised to disulphides, forming partly insoluble compounds. The resulting disulphides can be reduced back to the thiols. The ability of polythiols to pass into disulphides and the reverse process open up great prospects for the application of HS-containing polymers as ion- and electron-exchange resins. For example, the polythiol obtained by reaction (1) adsorbs mercury ions in the presence of Mg^{2+}.

It has recently been shown experimentally that polymeric thiols can initiate the thermal decomposition of diazoaminobenzene and the dehydrogenation of hydrazo compounds.

The soluble derivative of keratin — keratein — evidently possesses analogous properties. Keratein is obtained by the action of a 7–10% solution of sodium sulphide or hydrosulphide on finely ground keratinous waste from the wool, leather, and meat-processing industries[28]. The reaction between keratin and sulphides at 20° leads to complete dissolution of the protein:



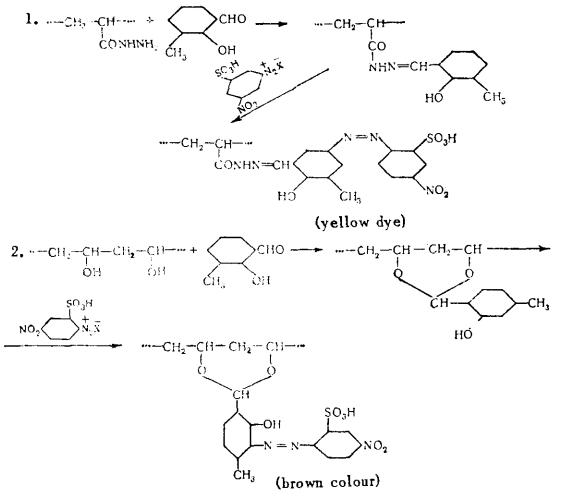
Keratein is readily soluble in water, dilute alkalis, and cuprammonium solutions, from which it can be obtained as films and fibres. Dilute (0.1–0.5%) solutions of H_2O_2 convert keratein into "pseudokeratin":

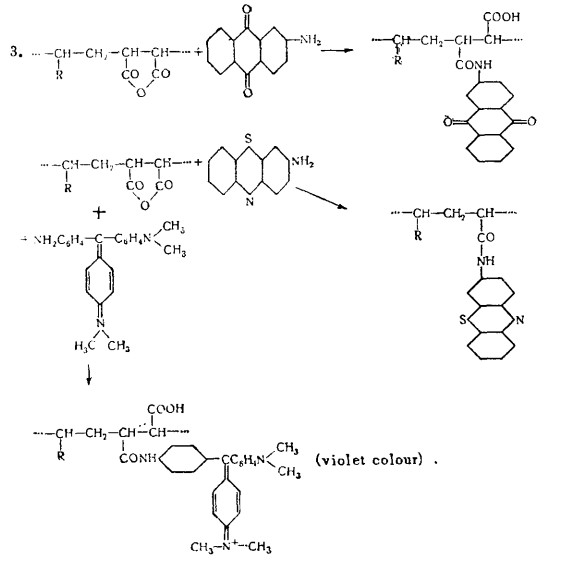


Keratein is of technical interest as an extremely effective and cheap stabiliser for emulsions, a detergent, a casein substitute in latex-protein impregnating compositions, and as a raw material for the production of films, plastics,

and fibrous materials[28,29]. In conformity with the properties of polymeric thiols noted above, it may be assumed that keratein will possess selective ion-exchange properties.

Other reactions of functional groups in macromolecules can be used to give polymers the properties of dyestuffs. Derivatives of carboxyl- and hydroxyl-containing polymers can be converted into polymeric dyes by the following methods[30]:

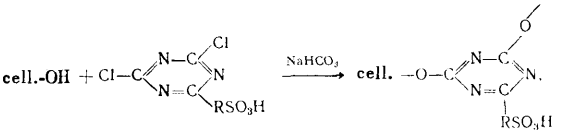




Since these compounds contain phenolic hydroxyl and a sulpho group, they are soluble in water. But their solubility can be adjusted by changing the proportions of polar, chromophoric, and hydrophobic groups in copolymers. Development on these lines will evidently lead to the production of a large range of chemically coloured polymeric fibres, films, and plastics.

Some polymeric dyes [e.g. those obtained by reactions (3)] possess oxidation-reduction properties, which suggests their possible use as electron-exchange resins.

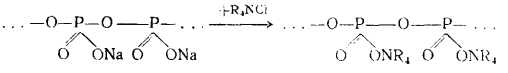
The presence of reactive OH groups in the cellulose molecule makes it possible to solve the problem of obtaining fast colours by using dyes which combine chemically with the fibre. Water-soluble dyes containing groups which can react with cellulose at pH > 7 may be used. Among these are the Procion (ICI) reactive dyes containing reactive cyanuric chloride groups in the molecule[31,32]. When cellulose fibres are treated with aqueous solutions of Procion dyes at pH > 7, the following reaction occurs[31]:



where R is the dye radical.

The chemical modification of cellulose has been discussed in detail in several exhaustive reviews[32,33].

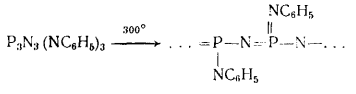
Little works has been published on the reactions of inorganic polymers, but it is worth mentioning results on the polymer-like changes that salts of polyphosphoric acid undergo[34]. Replacement of alkali cations in the polyphosphates by organic ions (trimethylammonium, benzyldimethylammonium) yields water-insoluble, heat-resistant, flexible polymers. The synthesis of such polyphosphates can be represented as



Polymeric phosphates are now under investigation as film-forming materials.

Interesting possibilities are opened up by the development of the chemistry of organic derivatives of polyphosphonitrilic chloride[30]. The phosphonitrilic chloride, formed by the interaction of ammonium chloride and PCl_5, is a mixture of cyclic trimers and tetramers of general formula $[Cl_2P:N]_{n=3,4}$. On heating to 300° phosphonitrilic chloride is polymerised, the ring opening to form a rubber-like product which crystallises at room temperature.

In order to obtain heat-resistant products not containing labile chlorine and remaining in an amorphous state over a wide range of temperatures, the synthesis of organic derivatives of polyphosphonitrilic chloride has been investigated[35]. Alcohols, phenoxides, organic acids, amines, and amides have been tested as reagents. The reaction of phosphonitrilic chloride with substituted anilides yields products which form thermoplastic polymers on heating:



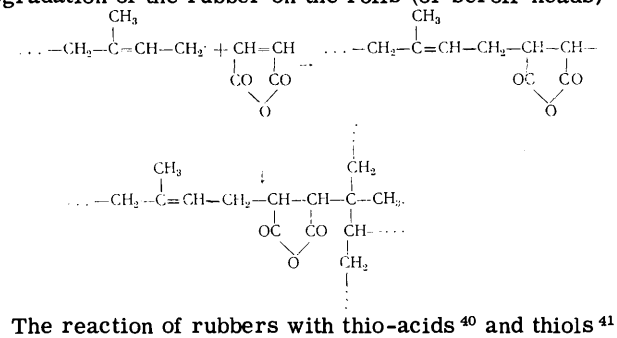
These derivatives of polyphosphonitrilic chloride melt above 300° and can be worked into films and plastics. Their impact strength can be improved by combining them with more elastic organic or organometallic polymers.

3. Addition to Double Bonds in Macromolecules

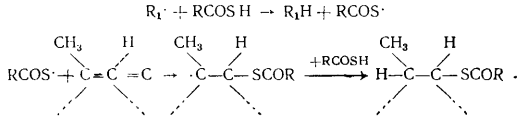
The presence of reactive double bonds in natural and synthetic rubber offers great opportunities for the chemical modification of these polymers. Hydrochlorinated rubber is widely used in industry for the production of film-forming materials; halogenation products of rubbers are employed in varnishes, adhesives, and plastics[15].

As long ago as 1938 it was shown that when toluene solutions of rubber containing a small amount of benzoyl peroxide and maleic anhydride are heated, the latter reacts with the rubber with the formation of rubber-like or rigid polymers[36]. This process was later carried out in the absence of solvents by masticating a mixture of rubber and maleic anhydride, acrolein, or acetylenedicarboxylic acid in the presence of benzoyl peroxide. The product obtained by treating the unvulcanised or vulcanised rubber[37,38] contained only 3–4% of maleic anhydride but differed markedly in properties from the original rubber; it was insoluble in benzene, formed strong vulcanisates with the oxides of lead, zinc, and several other metals, and was less permeable to gases.

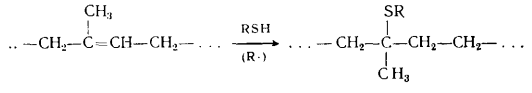
The mechanism by which rubber is modified when it is masticated with maleic anhydride has been little investigated as yet. It has recently been shown that the process is not to be regarded as a simple addition at the double bonds of the rubber and the monomer. It is more likely to be initiated by polymer radicals formed by mechanical degradation of the rubber on the rolls (or scroll-heads)[39]:



The reaction of rubbers with thio-acids[40] and thiols[41] is also of interest. For example, masticating natural rubber with 0.5–2 moles of thiobenzoic or trichlorothioacetic acid and an initiator yields a material of less regular structure, containing different types of units distributed in three dimensions[42]:



Rubbers modified with thio-acids are beginning to acquire practical importance for the production of a vulcanised rubber having increased resistance to frost and to oils and petrol[40]. A new type of elastomer developed not long ago also shows promise of practical application; it is obtained by treating latices of polybutadiene and other synthetic rubbers with thiols of low molecular weight (e.g. methanethiol) in the presence of azodiisobutyronitrile:



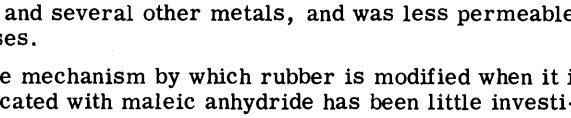
By varying the type of rubber, the thiol, and the degree of unsaturation, it is possible to obtain elastomers with various physical and mechanical properties[41].

When the quantity of thiol reacting is increased (raising the saturation to 85%), stronger and fairly elastic modified rubbers are obtained, having lower gas permeability, increased resistance to ageing, and greater stability to ozone, heat, solvents, and γ-radiation.

III. CHAIN GROWTH BY THE INTERACTION OF TERMINAL GROUPS OF MACROMOLECULES (BLOCK POLYMERISATION)

Reaction of terminal groups and active centres of macromolecules with polymerisable monomers, polymeric radicals, or terminal functional groups of oligomers yields linear or three-dimensional products of higher molecular weight.

When blocks differing in composition, structure, or spatial arrangement react, block copolymers are formed:



Block copolymers are thus isomers of the corresponding irregular copolymers. The presence in block copolymers of comparatively large (10–1000 Å) sections built up from units of the same type results in a kind of summation of the properties of the polymers involved in the copolymerisation.

The term "block copolymerisation" does not indicate the mechanism by which high polymers composed of segments of different types, or blocks, are formed. Both polyaddition and polycondensation processes, participating in chain growth by reaction of the end groups or active centres of macromolecules, are to be included among reactions of this type. It would be more correct to distinguish block copolymerisation and block co-condensation. These processes should be regarded as covering a far greater range of reactions than hitherto accepted. Indeed, it is now considered that such reactions occur in the synthesis of linear polymer[43,44]. Analysis of available experimental results shows, however, that, when end groups or active centres of macromolecules react either with themselves or with substances of low molecular weight, the formation of three-dimensional as well as linear structures is possible.

The extremely limited results so far available on the properties of three-dimensional block copolymers show that these substances possess several extremely important properties, determined by their spatial structure and the nature of the polymeric blocks involved in the reaction. We therefore consider it appropriate to examine separately synthetic methods, properties, and fields of application of linear and three-dimensional block copolymers. Such a classification is, of course, arbitrary in character, since in several cases synthesis of block copolymers may yield polymers both of linear and of three-dimensional structure.

1. Synthesis of Linear Block Copolymers

A. Mechanochemical methods. The formation of polymeric radicals by the mechanical degradation of high polymers was assumed in several papers published between 1930 and 1940[42-44]. But the possibility of using such macroradicals for the controlled synthesis of block copolymers has been investigated only since 1955[45-47]. The development of mechanochemical methods of synthesising block copolymers has enabled some important questions relating to the modification of polymeric materials to be solved; the general theory of the results obtained has been discussed, and they have been summarised in several reviews[49-51].

The mechanism and kinetics of chemical processes induced in polymers by mechanical means are undoubtedly of

fundamental significance in the mechanochemistry of compounds of high molecular weight, but at the present time investigation of this important problem is only in its initial stages.

Until recently a radical mechanism for the degradation of macromolecules by ultrasonic vibrations, by roller milling, masticating, mechanical grinding, and by repeated freezing has been demonstrated only by indirect methods (effect of acceptors on rate of degradation, initiation of polymerisation, formation of block copolymers); such methods cannot definitely confirm the formation of macroradicals, and give no idea of their life or chemical reactivity. In this connection great interest attaches to an investigation of the electron-paramagnetic-resonance spectra of the products formed by comminuting vitrified carbon- and hetero-chain polymers in an inert atmosphere over a wide range of temperatures (from -196° to +20°)[52].

When vitreous polyethylene, polystyrene, and several other carbon-chain polymers are ground in an eccentric mill for 15–20 min, a sharp drop (by a factor of 8–10) is observed in the value of $\bar{p}_{av}$ for the polymer, and paramagnetic-resonance spectra characteristic of radicals are produced. Radicals are also detected when fused quartz is ground, which points to a radical mechanism for the degradation of vitrified polysiloxanes. The concentration of paramagnetic species is in all cases of the order of 10^{17} per gram. After ground specimens of polyethylene (or polystyrene) have been thawed out and kept at room temperature, the intensity of the paramagnetic-resonance signal has almost vanished after 5–7 min. This important fact indicates that, in the case of linear polymers, recombination can occur even at temperatures below the vitrification temperature.

The intensity of the signal from ground fused quartz remains practically unchanged when specimens are maintained at 20°, and heating the degradation product of quartz to 40° leads to only a slow decrease in intensity, which points to the long life of three-dimensional macroradicals.

The electron-paramagnetic-resonance spectra of breakdown products of polymers obtained with a conical milling cutter also showed considerable concentrations of macroradical in the particles of the ground material. These investigations showed that macroradicals formed by milling polycaprolactam recombined rapidly even at 77°K.[53]

The most widely used mechanochemical method of modifying polymers is to work mixtures of polymers or polymer–monomer compositions on rolls, and ordinary and scroll-head masticators[54,55].

On mastication of polymers and polymer–monomer mixtures on rolls and in mixers of the Banbury type at temperatures as low as possible in an inert gas atmosphere, and sometimes even in the presence of air, block copolymers are formed which combine the properties of the polymers involved in the reaction.

The mastication of block and emulsion polystyrene mixed with polyisobutylene, butyl rubber, Butvar, polychloroprene, polybutadiene, and butadiene-styrene (SKS-30) and butadiene-acrylonitrile (SKN-18, SKN-30) rubbers has been investigated. By masticating mixtures of polystyrene with SKS-30 or SKN-18, a material is obtained having an impact strength greater than that of polystyrene by a factor of 4–5. The proportions of the rubber cannot conveniently be increased above 20–25%, since a great part of the elastomer would then remain uncombined with the polystyrene, which would diminish the strength characteristics and lower the vitrification temperature of the material[49].

The formation of block copolymers by the simultaneous mastication of polystyrene and a rubber is confirmed by results on the thermomechanical properties, solubility, and turbidimetric titration of a product containing combined rubber, and also by the fall in strength of the material observed on adding on to the rolls a radical acceptor (I_2) and certain dyes (pigment yellow, Bordeaux lake, etc.)[49]. Since some dyes contain reactive hydrogen or halogen atoms in the molecule, they can evidently act as fairly strong acceptors for macroradicals, and thus hinder the formation of a block copolymer.

High-strength plastics based on polystyrene or styrene–acrylonitrile copolymers modified with butadiene-styrene or butadiene-acrylonitrile rubber are used in the manufacture of refrigerator bodies, facing tiles, components of sanitary equipment, and other articles for a wide range of uses.

Treatment of mixtures of polymers and polymer–monomer compositions in a scroll-head masticator has been successfully used to obtain block copolymers of natural and synthetic rubbers[55,56], and also for the copolymerisation of rubbers with monomers (methyl methacrylate, acrylonitrile, acrylic acid, *p*-divinylbenzene, etc.[57]).

Raising the temperature of mastication was found to lower the rate of degradation of the polymer and hence the yield of macroradicals and block-graft copolymers formed with their aid. In spite of the relatively low activation energy of mechanochemical block copolymerisation, the activities of the macroradical and the monomer play a significant part in controlling the process[57].

Thanks to the work of Soviet investigators[58], the design of the scroll-head type of masticator has recently undergone considerable changes. By the simultaneous processing of mixtures of polymers and polymer–monomer compositions on the improved design of masticator, methods have been worked out for obtaining block copolymers of acrylonitrile rubber with phenol-formaldehyde and epoxy resins, coal-tar pitch, etc. The resulting block copolymers differ from the initial polymers in thermomechanical properties and solubility, and possess a combination of important physicomechanical properties (e.g. increased strength and adhesion, chemical stability, etc.)[59].

It was reported not long ago that several types of industrial scroll-head masticators are suitable for making block-graft copolymers by mechanical mastication of polymers[49]. Methods of modifying polymers during grinding, mastication, and extrusion are all included in the production cycle adopted for the processing of polymers. Owing to this circumstance, the introduction of such methods of modifying polymeric materials has great prospects in industry.

Apart from the study of mechanochemical changes in polymers and the synthesis of block copolymers in the condensed phase, work on methods of block copolymerisation by the action of ultrasonic vibrations on polymer solutions[49,60], by forcing the solutions through capillaries, and by vigorous stirring[61] also has much interest.

A new principle appears in the synthesis of block copolymers by cryolysis (freezing and unfreezing) of aqueous dispersions and solutions of polymers[45,62]. In this case degradation of macromolecules and formation of macroradicals are due to localisation of the internal pressure due to the phase transition at individual links in the polymer

chains. The cryolysis method has yielded block copolymers of starch and polystyrene with good emulsifying properties.

The mechanism of mechanochemical block copolymerisation is not yet finally established. The currently accepted view that formation of mechanochemical block copolymers is due solely to combination of polymer radicals does not, in the author's opinion, explain many experimental facts. Indeed, it has been noted above that the concentration of macroradicals formed by the ultrasonic degradation or mastication of polymers is of the order of 10^{-6}–10^{-7} mole g^{-1}. Yet the yields of block copolymers may reach 80–90% of the weight of degradable polymers. Such a disparity between the concentration of active molecules and the yield of block copolymer points to a chain mechanism for mechanochemical copolymerisation and cannot possibly be explained solely by radical combination or the possibility of graft copolymerisation by chain transfer from a polymer radical to macromolecules. It seems more probable that mechanochemical block copolymerisation involves degradation of polymer chains initiated by macroradicals. Mechanical degradation of polymers provides extremely favourable conditions for this reaction.

1. In view of the comparatively small number of macroradicals and the relatively large quantity of "non-radical" chains, the probability of interaction between polymer radicals and macromolecules is considerable.
2. During mechanical degradation macromolecules containing no unpaired electrons are activated by the distortion of valency angles due to the intense mechanical action on the polymer.
3. The rate of initiated degradation must be proportional to the concentration of macroradicals [R·] and "non-radical" macromolecules [P]: $v = k[R\cdot][P]$. As a result, even with small values of [R·] but large values of [P], initiated degradation may be quite intense. Block copolymers are formed, and new macroradicals arise, which further extend this chain process.

According to our suggested mechanism, mechanochemical block copolymerisation occurs as follows.

1. Production of active chains:

$$R{-}R + m{-}m \rightarrow R\cdot + m\cdot .$$

2. Chain growth:

$$R\cdot + m{-}m \rightarrow Rm + m\cdot, \text{ etc.},$$
$$m\cdot + R{-}R \rightarrow Rm + R\cdot .$$

3. Chain termination:

(*a*) by recombination:

$$R\cdot + m\cdot \rightarrow Rm,$$
$$m\cdot + m\cdot \rightarrow m{-}m,$$
$$R\cdot + R\cdot \rightarrow R{-}R;$$

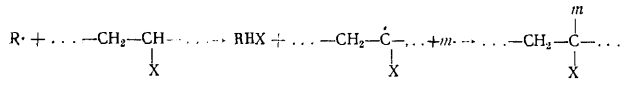
(*b*) by disproportionation:

$$R\cdot + R\cdot \rightarrow RH + \text{olefine},$$
$$R\cdot + m\cdot \rightarrow RH \text{ (or } mH) + \text{olefine};$$

(*c*) by reaction with the medium, the walls of the vessel, or impurities:

$$R\cdot + AX \rightarrow RX + A\cdot, \quad A\cdot + A\cdot \rightarrow A{-}A.$$

If the macromolecules contain bonds which can interact with macroradicals, the initiated degradation may be accompanied by a chain-transfer process, leading to the formation of branched macromolecules:



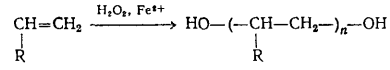
The probability of such a process is governed by the activity of the macroradical, the chemical nature of the polymer, and the conditions of mechanical degradation.

When a polymer undergoes mechanical degradation in the presence of a sufficiently active monomer, block copolymerisation occurs also by a radical-chain mechanism. However, the role of initiated degradation is then reduced to a minimum, since the dominant reaction is the macroradical-initiated polymerisation of the monomer.

The suggested mechanism for mechanochemical block copolymerisation explains the apparent discrepancy between the concentration of macroradicals and the yield of copolymers; it also accounts for the well-known fact that not all pairs of polymers can form block copolymers under conditions of mechanical degradation. It also readily explains the inhibiting effect of active acceptors of free radicals, and several other experimental facts.

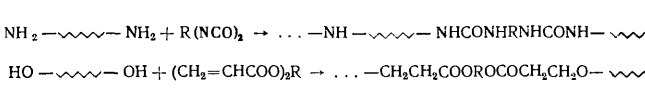
B. Chemical methods. General information on the synthesys of linear block copolymers by chemical methods, their properties, and their fields of application has been given in several reviews [18,43,65]. Chemical methods of obtaining block copolymers generally involve two stages; firstly the synthesis of polymeric blocks, which are macromolecules containing reactive functional groups at the ends of the chain, followed by reaction of the resulting products either with chemically different polymeric blocks or with monomers. For example, reaction of the terminal hydroxyls of polyoxypropylene (degree of polymerisation 20–80) with ethylene oxide yields a block copolymer of the composition $HO{-}[C_2H_4O]_n{-}[C_3H_6O]_m{-}[C_2H_4O]_n{-}OH$. At the present time block copolymers of propene and ethylene oxides are acquiring industrial importance as emulsifiers and cross-linking additives ("Pluronics").

The starting blocks may be synthesised by either polyaddition or polycondensation. In the former case, oxidation-reduction polymerisation of unsaturated monomers in aqueous medium yields carbon-chain polymers with OH end groups:



The synthesis of blocks by polycondensation of an excess of a glycol or an amine with a dicarboxylic acid yields polymers having either OH or NH_2 end groups. Appropriate proportions of a diisocyanate (in the preparation of polyurethanes) or of epichlorohydrin (in the synthesis of polyepoxides) give macromolecules with terminal isocyanate or ethylene oxide groups.

The polymeric blocks obtained by one of these methods are used to prepare various block copolymers with diisocyanates (hexamethylene diisocyanate, *m*-tolylene diisocyanate, etc.), diepoxides, diketens, tetrafunctional acrylates, etc. The principle underlying such block copolymerisation is illustrated by the following schemes [18]:



Block copolymerisation leads to vitreous or elastic products with average molecular weights exceeding those of the original blocks by a factor of 10–15. Linear block copolymers are of particular interest for the synthetic-fibres industry, since the degree of crystallinity of the polymer can be controlled by appropriate combination of crystalline and amorphous blocks. In this connection, block copolymers of poly(ethylene glycol terephthalate) (Terylene, Dacron) with poly(ethylene oxide) (Carbowax) are worthy of serious attention. This type of block copolymer contains both polyester blocks with the structure



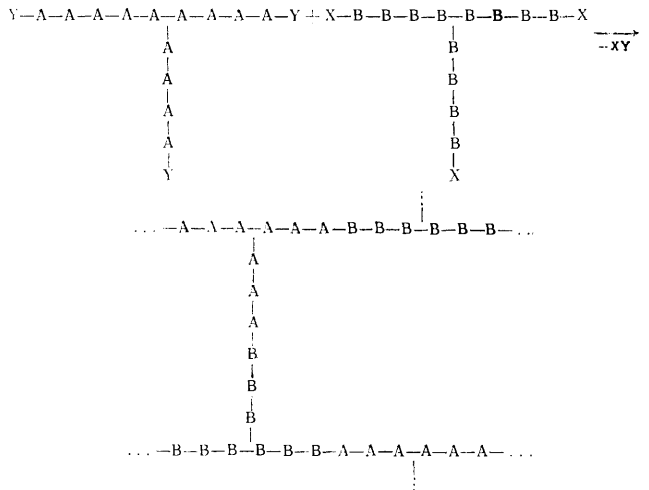
and also flexible and hydrophilic portions of poly(ethylene oxide) chains. The combination of such contrasting segments confers on the polymer considerable strength, extensibility, elasticity, and increased ability to absorb water.

2. Three-Dimensional Block Copolymers

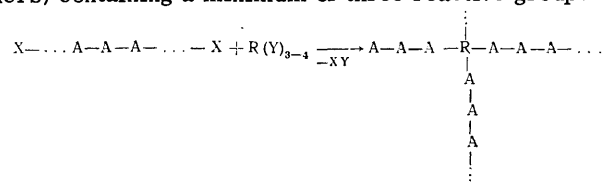
Three-dimensional block copolymers are of great theoretical and practical interest. They may be expected to combine the resistance to heat and solvents peculiar to three-dimensional structures with a wide range of other properties (e.g. elasticity, chemical stability, adhesion, etc.) contributed by the polymeric blocks involved in the reaction.

On the basis of the above definition of block copolymerisation as a method of synthesising substances of high molecular weight by reaction between the terminal groups of polymeric blocks, the following principles may be set out for the synthesis of three-dimensional block copolymers.

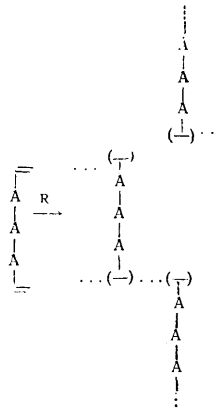
Type 1. Polymerisation or copolymerisation of branched blocks containing more than two terminal active centres or reactive groups:



Type 2. Reaction between linear (or branched) blocks and substances of low molecular weight (in the limit, monomers) containing a minimum of three reactive groups:



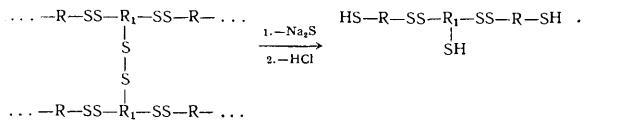
Type 3. Polymerisation of blocks having bifunctional groups capable of either chain or stepwise polymerisation at the ends of the chains:



Reactions of type 1. Blocks of branched structure may be prepared by mechanical or chemical degradation of three-dimensional polymers. Thus when vulcanisates of natural rubber (light crepe, smoked sheet) or synthetic rubber (butadiene-styrene, butadiene-acrylonitrile, butyl) are masticated in a laboratory mixer with a spiral rotor, mechanical degradation occurs and strongly branched, partly cross-linked macromolecular fragments are formed[66]. Such products swell in monomers (methyl methacrylate, methacrylic acid, styrene).

When vulcanisates which have been swollen in monomers are masticated in an atmosphere of nitrogen, incompletely soluble or insoluble copolymers are produced; these can be moulded as plastics and are more or less strong and elastic according to the quantity of combined polymer[46,66].

The use of degraded vulcanisates to obtain modified rubbers and high-strength plastics is practically important, since it enables reclaimed rubber to be used in making economically practicable polymers. The synthesis of branched blocks by the chemical degradation of network structures is no less promising. Thus, when a suspension of Thiokol, obtained by co-condensation of dichlorodiethyl formal, small amounts of trichloropropane, and sodium disulphide, is treated with sodium sulphide or hydrosulphide, liquid mercapto-polysulphides are obtained, which under appropriate conditions can form rubber-like materials[67].



The liquid mercapto-polysulphides obtained, have viscosities of 0.5–450 poises and mean molecular weights of 3000–4000, depending on the concentration of sodium disulphide and the composition of the bath. The action of organic or inorganic peroxides (cumenyl peroxide, acetyl peroxide, PbO_2, NO_2, etc.), alone or mixed with amides (diphenylguanidine), and also of atmospheric oxygen in the presence of driers, converts the liquid mercapto-polysulphides at 20° into rubber-like substances[67].

The hardening of the mercapto-sulphides evidently occurs by a radical mechanism, and can be represented to

a first approximation by the scheme

$$R(SH)_2 + R_i \rightarrow HSRS\cdot + R_iH$$

$$2HSRS\cdot \rightarrow HSRSSRH \xrightarrow{+R_i} HSR(SSRSSR)_nSH,$$

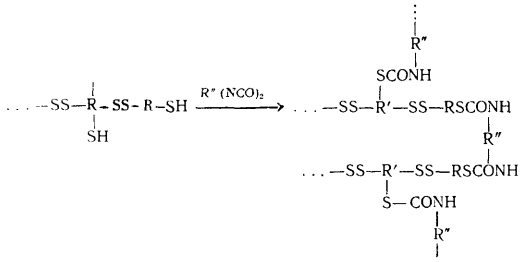
where R is the poly(alkyl sulphide) chain of liquid Thiokol.

Activation of the terminal mercapto groups of the branched chains and their interaction results in the observed transition from viscous liquid products to vulcanised rubbers. The rubber-like materials possess high resistance to petrol and oils, and are suitable for use over quite a wide range of temperatures (from -54° to +150°).

The ultimate tensile strength of filled vulcanisates (containing carbon black, PbO, TiO_2) is 80–90 kg cm^{-2} at an extension of 200–300%. Compositions based on liquid Thiokols have been successfully employed for the production of moisture- and gas-impermeable films and coatings resistant to weathering, the internal linings of petrol tanks, etc.

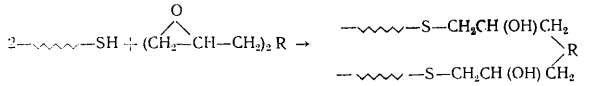
Liquid polysulphides can be used to plasticise polyvinyl chloride and also in compositions with phenol-formaldehyde resins[1,67].

The synthesis of three-dimensional block polymers by the interaction of branched and linear blocks with monomers opens up great opportunities for modifying the properties of polymers. In this connection the copolymers of liquid Thiokols with diisocyanates must be mentioned:



Diisocyanate-polysulphide copolymers possess high adhesion to metals, elasticity, frost-resistance, and resistance to oils and solvents.

The epoxy-polysulphide copolymers formed by reaction between polymeric epoxy compounds[68] and polysulphides in the presence of polyamines (triethylenetetramine, tris(dimethylaminomethyl)phenol, etc.) are becoming important. According to the relative proportions of the initial components and the quantity of hardener, these compositions can be hardened at 20°–100°. The chemistry of the reactions can be represented by the scheme

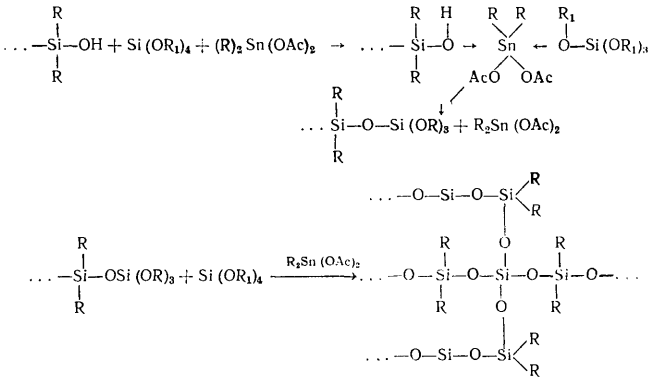


Before hardening, epoxy-polysulphide compositions are less viscous than the original polysulphide, but after hardening they form elastic products possessing high adhesion, and resistance to water, solvent, and ageing. The strength of such materials depends on the type of epoxy and polysulphide resin and the relative proportions of the components in the resin composition.

Epoxy-polyester resins are conveniently used in the preparation of adhesives, sealing compounds, protective coatings, binders, etc.

Reactions of type 2. Three-dimensional block copolymerisation of linear blocks with multifunctional monomers was recently used to convert viscous liquid polydimethylsiloxanes (M_{av} = 10 000–50 000) into rubber-like products, and also to vulcanise organosilicon rubbers at room temperature[61,69-71]. The principle of the method is the reaction of the terminal hydroxyl groups of the polydimethylsiloxane with tetraethyl orthosilicate in the presence of organotin catalysts of the type R_2SnOAc, where R is an alkyl or an aryl group, and Ac is an acyl group.

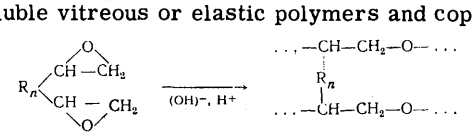
The mechanism of the reaction can be represented by the scheme[69]



It is evident from this scheme that the new method of polycondensation opens up a prospect of modifying polysiloxanes. Indeed, with the aid of this principle, various block copolymers differing in chemical nature from polysiloxanes, as well as other classes of oligomeric substances containing hydroxyl or carboxyl groups at the ends of the chains, can be obtained. The preparation of linear, three-dimensional, or branched block copolymers by interaction of polymeric blocks with tri- and multi-functional monomers is an extremely promising general method for the synthesis of such compounds.

This interesting reaction could appropriately be called a "multiplication reaction". The recently described method of "doubling"[72] is evidently merely a particular case of the general principle of block copolymerisation. However, the method of doubling, in the form proposed by Kern and his coworkers, can have only a limited application for decreasing the polydispersity of certain types of polymers.

Reactions of type 3. Let us consider the three-dimensional polymerisation of blocks containing, at the ends of the chain, groups which can undergo chain or stepwise polymerisation. Among such oligomers are epoxy-polyethers, obtained by the action of epichlorohydrin on dihydric phenols, glycols, or diamines[73,74]. In the presence of bases at room or slightly elevated temperatures (60°–110°), epoxy-polyethers are converted into infusible and insoluble vitreous or elastic polymers and copolymers:



The physical and mechanical properties of polyepoxides are largely determined by the chemical nature and the mean degree of polymerisation of the blocks used.

The ability of epoxy-polyethers to copolymerise with various hydroxyl-, amino-, and carboxyl-containing polymers (phenol-aldehyde resins, polyamides, polyesters, etc.) has enabled far-reaching modifications to be made in the properties of various polymeric materials. The large

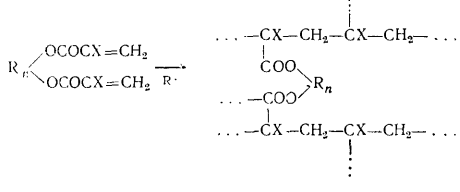
variety of materials obtained from epoxy-polyethers have found widespread application as binders for reinforced plastics, casting resins, plastic foams, coatings, sealing compounds, adhesives, etc.[74] The polyester-acrylates, a new type of oligomeric substances able to undergo three-dimensional polymerisation, which have been developed in the USSR, offer equal possibilities[75]. Polyester-acrylates are synthesised by controlling chain growth during polyesterification by adding monobasic methacrylic or acrylic acid to the reaction mixture. By analogy with a reaction known to occur by a radical-chain mechanism, we have termed this reaction "condensation telomerisation".

The course of the reaction can be represented by the general scheme

$$R(OH)_2 + R_1(COOH)_2 + CH_2=\underset{\displaystyle X}{\overset{\displaystyle |}{C}}-COOH \rightleftarrows$$
$$\rightleftarrows CH_2=\underset{\displaystyle X}{\overset{\displaystyle |}{C}}-CO(OROCOR_1COO)_nROCOC=\underset{\displaystyle X}{\overset{\displaystyle |}{C}}=CH_2,$$

where R and R_1 are alkyl or aryl radicals, and X = H, CH_3, Hal. When the proportion of methacrylic acid is reduced from 2.2 moles to 0.1 mole per mole of dibasic acid, polyester-acrylates are obtained with $\bar{n}$ = 1–20 and mean molecular weights reaching 4000–5000[76]. When the reaction of the monomers involves more than two functional groups, branched oligomeric polyester-acrylates are formed.

Investigations of the three-dimensional polymerisation of polyester-acrylates have shown that, in the presence of initiators, these viscous liquid products can be converted into infusible vitreous or ebonite-like polymers both at room temperature and above[77]:



where R_n is a polyester radical. The various polyester-acrylates can form block copolymers both among themselves and with bi- and multi-functional monomers (styrene, methyl methacrylate, acrylonitrile, etc.).

Increase in the distance between the acrylate groups in polyester-acrylates produces a sharp decrease in the contraction accompanying polymerisation (when $\bar{n}$ = 4 the volume contraction is 0.3–0.5), an increase in the impact strength and in the hardness of the three-dimensional polymer, and also an improvement in the adhesive properties; this opens up a prospect for their use as binders, adhesives, coatings, sealing compounds and pastes, etc.[76]

IV. REACTIONS OF GROUPS AND ACTIVE CENTRES WITHIN MACROMOLECULES ACCOMPANIED BY CHAIN GROWTH

Reaction of active centres or functional groups, distributed along the chains of macromolecules, with substances of low molecular weight, monomers, macroradicals, or polymers can give rise to branched or three-dimensional structures, differing in the chemical character and in the structure of the main chain and the side branches. If these processes result in growth of the side branches, they are to be regarded as graft polymerisation and to be distinguished from the conversion of macromolecules into spatial structures by the action of substances of low molecular weight which are incapable of homopolymerisation. Chemical reactions of macromolecules of the latter type are conveniently included among "cross-linking" reactions.

1. Graft Polymerisation

The fundamental principles of radical-chain graft copolymerisation were first worked out in the USSR in 1946[78] and somewhat later in France[79].

By graft copolymerisation a very extensive modification of the properties of polymers can be made in desired directions, since the introduction of polymeric blocks of 50–100 Å in the form of side branches or cross-linking chains, similarly to block copolymerisation, results in a summation of the properties of the substances involved in the reaction.

The growth of side chains can occur both by radical or ion-chain polymerisation and by direct stepwise (migration) polyaddition or polycondensation[43,65]. Synthesis of graft copolymers by radical-chain methods can be accomplished by chain transfer during polymerisation of a monomer in the presence of a polymer, by copolymerisation of branched polymers containing double bonds in the side chains, and also by the so-called "two-stage method", based on the introduction into the polymer of peroxide, perester, diazonium, and other groups which can break down to form active centres[43].

The use of polycondensation or stepwise polyaddition for the synthesis of graft copolymers is possible when the macromolecules of the polymer contain, in the main chain or in the side branches, reactive functional groups (OH, SH, NH_2, COOH, etc.) or groups which can add on a proton with formation of new covalent bonds (isocyano groups, three- and four-membered heterocycles, etc.). Graft copolymers are then formed by the reaction with the corresponding monomeric substances or with polymeric blocks containing reactive end groups.

2. Synthesis of Graft Copolymers by Chain Transfer

This is the easiest way to modify the properties of polymers. The separate stages in the formation of a graft copolymer by chain-transfer methods can be represented by the following scheme:

1. Formation of active centres:

   (*a*) by decomposition of the initiator:

   $$RR \rightarrow R\cdot + R\cdot;$$

   (*b*) by interaction of R· with R_nH macromolecules:

   $$R\cdot + R_nH \rightarrow RH + R'_n\cdot.$$

2. Chain growth:

   (*a*) by homopolymerisation of the monomer:

   $$R\cdot + M \rightarrow R-\sim\sim\sim\cdot;$$

   (*b*) by graft copolymerisation:

   $$R'_n\cdot + M \rightarrow R_n-M-M-M\cdot.$$

3. Chain termination:

   A.

   (*a*) by recombination of growing homopolymerisation chains:

   $$2R-M-M-M-M\cdot \rightarrow (R-M-M-M-M)_2;$$

(*b*) by recombination of dissimilar macroradicals:

$$R{-}M{-}M{-}M{-}M\cdot + R_n \cdot \rightarrow R{-}M{-}M{-}M{-}M{-}R_n \quad ,$$
(branched graft copolymer)

$$2R_n{-}M{-}M{-}M{-}M\cdot \rightarrow (R_n{-}M{-}M{-}M{-}M)_2; \quad 2R_n \cdot \rightarrow (R_n)_2 \; ;$$
(three-dimensional graft copolymers)

B. by disproportionation:

$$R_n(M)_n + R_n(M)_m \rightarrow R_n(M)_n + R_n(M)_m .$$

In this case processes leading to the formation of graft copolymers are seen to be accompanied by homopolymerisation.

A chain-transfer reaction is characterised by a chain-transfer constant, representing the ratio of the velocity constant for transfer of the chains to that for their growth. When polymerisation is carried out in solution, the solvent takes part in chain transfer. Thus, with isopropylbenzene the chain-transfer constant is 0.8×10^{-4} at 60°, and 2×10^{-4} at 100°. The growth of the chains occurs 10 000 times as rapidly as their transfer, the activation energy for chain transfer being considerably greater than that for chain growth; in the case of isopropylbenzene the difference amounts to 5.5 kcal. A kinetic study of chain transfer shows that, in order to bring it about, a high temperature and a high concentration of polymer in the solution must be maintained. The high viscosity of a concentrated solution of a polymer considerably reduces the probability of chain termination, thus favouring the reactions of chain transfer and chain growth; numerous experiments have shown that high yields of graft copolymers are achieved under these conditions. Apart from the conditions under which transfer is carried out, the chemical nature of the polymer and the monomer, which determines their polarity and reactivity, and also the presence of steric hindrance, is an extremely important factor in graft polymerisation. Available data show that the intensity of graft copolymerisation decreases in the following sequence, according to the chemical nature of the monomer: vinyl chloride > vinyl acetate > styrene; and according to the chemical nature of the polymer: polyvinyl chloride > polyacrylonitrile > polyvinyl acetate > > polystyrene.

Although the method of chain transfer does not allow graft copolymers to be prepared free from admixture with homopolymers, it has been widely employed in practice. Thus, by the polymerisation of a series of monomers (acrylates, vinyl acetate, etc.) in a polyvinyl chloride latex, graft copolymers were obtained which combined the adhesion and atmospheric stability characteristic of acrylates and polyvinyl acetate with the increased resistance to abrasion, the action of chemicals, water, petrol, and oils of polyvinyl chloride. Such copolymers are used as protective coatings and film-forming materials[80].

Graft copolymers of rubbers and polystyrene or poly(methyl methacrylate) are widely used in industry. Such copolymers may be synthesised both by polymerising the monomers in a latex of synthetic or natural rubber in the presence of water-soluble initiators (e.g. potassium persulphate), and by polymerising the monomer with the rubber either dissolved or swollen in it. Either elastomers or strong plastics may be formed, according to the relative proportions of rubber and monomer.

Rubber-like graft copolymers are formed, when styrene, methyl methacrylate, or acrylonitrile are polymerised in latices of natural or synthetic rubbers in the presence of hydroperoxides and aliphatic amines with 20–50% of the monomer[81,82].

The vulcanisation of graft rubbers yields rubbers possessing increased strength and resistance to weathering and rubbing. Such materials are produced on an industrial scale in the USA and in England. The great strength of unfilled graft rubbers opens up new prospects in the technology of gas-filled elastomers; lighter and stronger foam rubbers can be obtained, and they will evidently be competitive with elastic polyurethane foams in future[83].

In preparing plastics based on graft copolymers of rubber, the proportion of elastomer relative to monomer must not exceed 10%. Otherwise, polymerisation of styrene in the latex gives very low yields of graft copolymer. Impact-resistant material is obtained by introducing even as much as 30% of rubber[84]. Such material, however, possesses diminished hardness and greater residual deformation than polystyrene on compression and extension.

It has recently been shown experimentally that graft copolymerisation of styrene with rubber in bulk at 80°–170° gives a high yield of graft copolymer with 5–10% additions of rubber. From such rubber-modified polystyrene quite hard and elastic materials are obtained, which withstand impact loads 3–5 times as great as in the case of plastics based on polystyrene or its copolymers with acrylonitrile[85]. Graft copolymers of styrene with butadiene-styrene rubber are not inferior to the so-called "latex polystyrene" in dielectric properties, and considerably surpass it in strength characteristics, so that these products can be used for sheet materials, films, and casting resins.

Great developments in the principle of grafting by chain transfer are made possible by methods of initiating graft copolymerisation with γ-rays and fast neutrons[86,87]. The velocity of radiation-induced graft polymerisation depends on the intensity of irradiation, the dose, the temperature, the medium, the presence of sensitisers or inhibitors, etc. When γ-rays (^{60}Co) are used, exposure is generally carried out at room temperature or somewhat above (40°–50°) with an intensity of the order of 200 000–300 000 rep/h.

Radiation grafting methods are very promising and allow graft copolymerisation to be carried out on the surfaces of film materials (so-called "surface grafting")[87-89]. In the future it should be possible to work out systematic procedures for modifying the properties of the finished articles. When graft polymerisation is carried out on the surfaces of films, a very important factor, in addition to those noted above, is the diffusion of the monomer into the polymer and the distribution of the former between the phases in contact (polymer and solution)[89].

Diffusion of monomer into the initial polymer plays a large part in determining the structure and properties of the product obtained. It depends on the coefficients of diffusion of the monomer in the solution D_l and in the polymer D_p, and also on the Nernst partition coefficient K (the ratio of the concentration of monomer in the polymer to its concentration in the solution), which determines the equilibrium distribution of the monomer between the two phases. During diffusion such an equilibrium is established directly at the film–solution interface. Surface and bulk graft polymerisation are possible in systems in which the resulting concentration gradient of monomer in the films is not too great. The lower K and the greater D_p (compared with D_l), the smaller is the concentration gradient during diffusion. This condition is satisfied in the polyvinylpyrrolidone–acrylonitrile and polymethacrylic ester–acrylonitrile systems. With a high partition coefficient K and a low diffusion coefficient D_p, the concentration of monomer directly at the film

surface is high, and a considerable concentration gradient appears in the course of diffusion. In this case the surface of the film swells, and changes its original shape. A surface graft without change in shape of the polymer is possible in such a system if swelling of the film is carried out with low concentrations of monomer in the solution and the period of diffusion is restricted. Bulk graft polymerisation does not then occur. An example is the polymethacrylic ester–vinylpyrrolidone system[89].

Complications arise from the fact that the diffusion of monomer into the polymer is affected by the graft polymer obtained from the initial monomer which had diffused during irradiation. Subsequently the graft polymer acts in the diffusion process as a third phase having its own coefficients of diffusion and of partition with the solution and with the polymer within the film which has not yet undergone graft polymerisation. If the graft polymer is more readily soluble in the monomer than is the original polymer, the partition coefficient for monomer between solution and film increases, and at the same time diffusion of monomer into the interior of the film (which has not undergone graft polymerisation) slows down. The polyisobutylene–styrene system is of this type.

When the resulting graft copolymer is more soluble than original polymer in the monomer, the velocity and completenes of grafting are substantially affected by osmosis. This may possibly explain the increase in the rate of graft copolymerisation with increase in film thickness observed in several cases[89].

Formation of homopolymers is not excluded during irradiation of polymer films in a monomer medium. Contamination with homopolymer can be diminished by using aqueous dispersions of monomers, and practically eliminated (or reduced to a minimum) by the two-stage method of graft copolymerisation. The principle of this interesting process for radiation grafting on films is based on the comparatively long life of macroradicals formed by the irradiation of vitrified polymers[88]. This allows us to carry out separately irradiation and subsequent graft polymerisation on the surface of the irradiated polymer placed in a medium containing the monomer.

By applying radiation-grafting methods to a polyethylene–vinylcarbazole surface, materials are obtained which surpass the individual polymers in several properties; such copolymers have a higher softening point and a greater electrical resistivity than either unexposed or irradiated polyethylene, together with a greater impact strength than polyvinylcarbazole. When films of polytetrafluoroethylene (Teflon) are irradiated in the presence of styrene, a graft copolymer is formed on the polymer surface. A graft of 1–10% of styrene increases the adhesion of Teflon to polymers and to aluminium.

Interesting results are achieved in the radiation grafting of polyacrylonitrile to films of vulcanised polydimethylsiloxane[87]. Such a graft copolymer exhibits, together with the heat resistance characteristic of polysiloxanes, considerably less swelling in petrol, aromatic hydrocarbons, and other organic solvents.

Graft polymerisation at film surfaces can yield strong cation- and anion-exchange membranes of high exchange capacity. Cation-exchange membranes are prepared by sulphonating films of polyethylene containing a graft copolymer of polyethylene and styrene on the surface.

For anion-exchange membranes, polyvinylpyridine is grafted on the surface of a polyethylene film, with subsequent conversion of the pyridine groups in the side branches into quaternary ammonium bases.

A sulphonated film containing 20% of polystyrene grafted to polyethylene has a wet strength of 80.5 $kg\,cm^{-2}$. The strength of the industrial membrane Amberplex S-1 is 17.5 $kg\,cm^{-2}$. It may be assumed that the polyethylene restricts the swelling of sulphonated graft-copolymer membranes, and to a considerable extent determines the strength of such films[87]. A still greater increase in strength and stability towards aqueous solutions of electrolytes may be achieved by the graft copolymerisation of polyethylene films with divinylbenzene and its mixtures with styrene.

The widespread use of graft copolymerisation by ionising radiation is impeded by (1) difficulties associated with ensuring safety and controlling the process when working with γ-rays, and (2) lack of methods for eliminating side reactions, which result in degradation or cross-linking of the polymer macromolecules during grafting.

Recently, therefore, attention has been turned to the possibility of effecting graft polymerisation by means of ultra-violet radiation (λ = 254–280 mμ). When films of polyethylene containing benzophenone are irradiated in acrylonitrile medium, surface grafting occurs, producing an increase in hydrophilic character, a diminution in swelling in hydrocarbons, and a change in the adsorption of dyes by the polymeric film[90,91].

Grafting by means of ultra-violet radiation enables degradation of the polymer and formation of homopolymer to be avoided; together with its safety, this is the great advantage of the method.

3. Graft Copolymerisation of Polymers Containing Active Centres in the Macromolecules

In addition to the above methods based on chain transfer, processes of graft copolymerisation based on the introduction into the macromolecules of groups which readily form active centres of polymerisation are acquiring practical importance. Such groups are usually introduced by auto-oxidation[92], ozonolysis[93,94], direct chemical synthesis (e.g. by the reaction of polyacryloyl chlorides with alkyl hydroperoxides)[92,95], irradiation with X-rays or γ-rays in air, and electrolysis of polyacrylic acid or carboxyl-containing elastomers[96-97]. Among these a very promising method is based on separate ozonisation, with subsequent graft copolymerisation of a monomer and the ozonised polymer. Mild ozonisation enables grafts to be made on polymeric films and fibres[98]. The principle of the method consists in treating the film (polyethylene, polystyrene, etc.) at room temperature with ozonised oxygen and subsequently keeping the material in a solution or an emulsion of the monomer at an elevated temperature in an inert gas. Graft polymerisation occurs on the surface of the film, as a result of which its weight increases by 2–20%.

By grafting acrylonitrile on crystalline polyethylene, obtained by the Ziegler method, it is possible to reduce markedly its permeability to gases and to increase its stability to light. A graft of 15% of acrylic acid on polyethylene fibres and films yields materials which are stronger and more hydrophilic in character, and capable of being dyed with basic dyes.

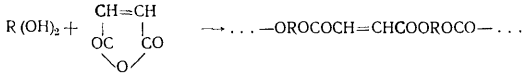
By using the ozonisation method, it has recently been possible to graft vinyl monomers on a polyamide[99] and to obtain graft copolymers of starch and polystyrene. Such

copolymers are prepared by ozonising an aqueous suspension of starch and subsequently polymerising styrene on the ozonised starch in an atmosphere of nitrogen at 70°–100°.[100] Depending on the relative proportions of starch and styrene and the duration of ozonisation, products were obtained with different physical and mechanical properties. These copolymers were shown to be excellent stabilisers for emulsions of water and styrene.

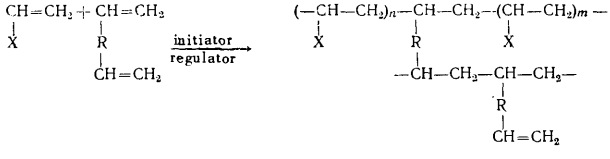
Ozonisation is also a very promising method for modifying the properties of many other natural polymers. Thus the ozonisation of cellulose (cotton fibre, viscose cord) enables an acrylonitrile graft to be made by treating the fibre or cord with a solution of the monomer in a high vacuum (10^{-6} mm Hg) on a boiling water bath[101].

4. Graft Copolymerisation of Unsaturated Polymers. Three-Dimensional Copolymers

Polymers containing double bonds in the main chain are prepared by polycondensation of α,β-unsaturated dibasic acids or their anhydrides (maleic, aconitic, itaconic, etc.) with glycols[102,103]:



Polymers containing double bonds in the side chains were first synthesised in the USSR (1946–1947)[104]. The method consists in principle in copolymerising unsaturated bi- and quadri-functional monomers under conditions which hamper the formation of three-dimensional structures. To avoid the formation of a network polymer, the process is carried out in a non-solvent medium (water, methanol, etc.) in the presence of an initiator and a regulator for the polymerisation process (an amine, a thiol, or a phenol)[104]. Allyl esters of dibasic acids can be used as the quadrifunctional monomers. This reaction can be represented as



The yield of soluble unsaturated copolymer is 75–85%. The content of double bonds is ~20–25% of the theoretical, which indicates that the copolymer macromolecules have a branched structure.

Compounds of high molecular weight containing reactive double bonds can be prepared also by esterifying hydroxyl-containing polymers with unsaturated acids or by etherifying them with unsaturated alcohols. Thus the reaction of cellulose or the so-called "secondary" cellulose acetate with methacrylic anhydride yields methacrylic or acetomethacrylic esters containing 0.1–1.0 methacryloyl group per glucose unit[105].

The initiated polymerisation of bi- or quadri-functional monomers in the presence of polymers containing double bonds generally yields insoluble three-dimensional graft copolymers. Such products are therefore most conveniently made not in advance but during the manufacture of various articles. Thus mixtures of poly(ethylene glycol maleates) with styrene and an initiator are employed as binders in the production of reinforced plastics, protective coatings, and insulating compounds[102]. Compositions based on polyacrylates or branched copolymers of acrylic esters and biscarboxyallyl ethers of ethylene glycols with polyester-acrylates or dimethacrylic esters of di- and poly-hydric alcohols have found practical application as adhesives and special pastes which harden at room or elevated temperatures (60°–80°). Such adhesives form strong joints between metals, and between metals and various non-metallic materials[76,106].

The three-dimensional graft copolymerisation of acetomethacrylic and nitromethacrylic esters of cellulose with acrylic and methacrylic esters is of considerable interest for the preparation of new types of plastics and protective coatings.

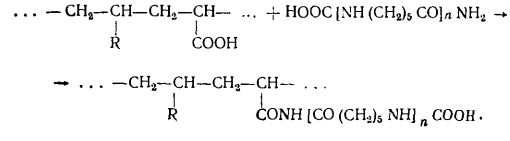
The surface methacrylation of cellulose fibres with subsequent surface grafting of acrylonitrile enables cotton cloth to be given improved crease-resistance and increased wet strength[107].

The development of the principle of three-dimensional graft copolymerisation, first worked out in the USSR in 1946, to remake polymer-monomer bonds in finished articles will in the future undoubtedly lead to new and more systematic methods for making casting resins, binders, protective coatings, gas-filled plastics, and other polymeric materials[104].

5. Synthesis of Graft Copolymers by Polycondensation and Stepwise Polymerisation

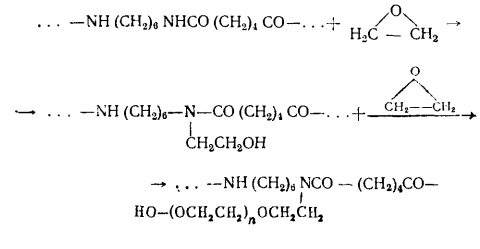
To obtain graft copolymers by polycondensation or stepwise polymerisation, polymers containing NH_2, COOH, OH, $CONH_2$, SH, and CHO groups are used[1,43]. As regards stepwise polymerisation, great interest attaches to polymers containing isocyano groups or epoxide or cyclooxabutane rings in the side chains[1,108].

When polyacrylic acid or copolymers containing carboxyl groups are condensed with polycaprolactam, copolymers of the following type are formed[109]:



Such copolymers possess an extremely wide range of properties, including moisture absorption, ability to take dyes, and increased resistance to light. Development of this process may yield extremely interesting graft copolymers of polyacrylonitrile and polycaprolactam.

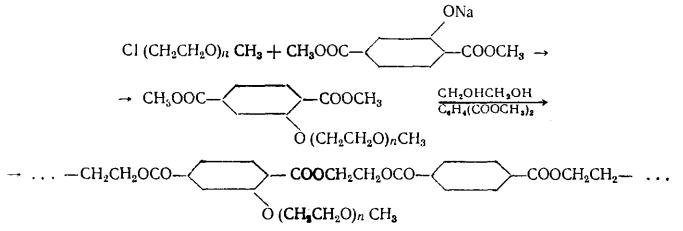
Stepwise graft copolymerisation is beginning to acquire practical significance for modifying the properties of nylon. Thus grafting polyethylene oxide side chains on polycaprolactam, 6,6-nylon, and other types of polyamides has enabled their moisture absorption and ability to take dyes to be improved without lowering the softening point or reducing the strength[110,111]. The nature of this reaction is evident from the scheme



The change in the hydrophilic character of nylon with its content of ethylene oxide units can be seen from the following data[110].

C_2H_4O content in nylon, %.	Moisture permeability, $g\,m^{-2}\,h^{-1}$.
10.6	3.13
32.0	31.0
42.2	32.3
49.5	52.8

A more hydrophilic Terylene has been synthesised by reaction of the methyl ether of polyethylene chlorohydrin with the sodium derivative of dimethyl hydroxyterephthalate and subsequent reaction of the resulting product with ethylene glycol and dimethyl terephthalate:



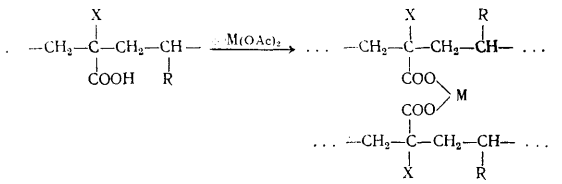
Three-dimensional graft copolymers can also be obtained by polycondensation and stepwise polymerisation methods. Such copolymers have been prepared[112] by the reaction of polymers containing a carboxyl or an amide group with caprolactam, and of polyamides with Resol resins, epoxypolyethers, and polyurethanes.

6. Cross-Linking Reactions

The presence in macromolecules of carboxyl, aldehyde, hydroxyl, sulphoxyl, isocyanato, amide, epoxy, and several other functional groups leads to various types of three-dimensional polymers, with increased heat resistance, strength, a permanent colour, selective ionic adsorption, ionic conduction, etc.

For example, as early as 1947 a process was suggested for converting carboxyl-containing polymers, obtained by copolymerisation of unsaturated acids with various monomers (methacrylates, acrylates, acrylonitrile, etc.), into an infusible and insoluble condition by reaction with bi- and multi-valent metal ions and with diamines[1,113].

Carboxyl-containing polymers, when mixed with oxides of bi- or multi-valent metals or their salts (stearates, oleates), react when pressed at elevated temperatures (120°–140°) to form three-dimensional structures:



The resulting material is infusible, withstands heating to 250°–300°, and is stable to the action of solvents. The physicochemical and mechanical properties of such polymers can be changed within wide limits by varying the chemical nature of the copolymer or the cross-linking metal oxides or salts. The inorganic oxides used to convert carboxyl-containing polymers into three-dimensional products can be replaced by glycols, polyhydric alcohols, diamines, or compounds of high molecular weight containing OH or NH_2 groups (partly hydrolysed polyvinyl acetate, polyvinyl acetal, polyamides[113]. This method has recently attracted the attention of investigators and technologists. For example, copolymers of butadiene and methacrylic acid are finding increasing practical application for the preparation of raw rubbers convertible into high-strength rubber by reaction of the COOH groups with metal oxides[114].

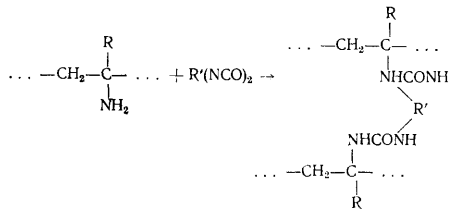
Copolymers of methyl methacrylate with methacrylic acid mixed with partly hydrolysed polyvinyl acetate are recommended as thermosetting coatings and binders which adhere well to metals, wood, and plastics. Compositions consisting of carboxyl-containing copolymers[115] (e.g. copolymers of butyl methacrylate with 5–10% of methacrylic acid) and hydroxymethyl derivatives of urea or melamine[116] are important in varnish technology.

Coatings based on such compositions, when heated at 80°–120°, acquire great hardness, elasticity, and adhesion to metals, glass, wood, etc. During the baking process the COOH groups of the copolymer react with the CH_2OH groups of the melamine or urea derivatives to form an infusible and insoluble polymer, which apparently has a three-dimensional structure.

Work on the preparation and application of carboxyl-containing polymers has led to the production of cation-exchange resins which can adsorb ions of the alkaline-earth metals; insoluble copolymers of polyacrylohydroxamic acid are employed as cation-exchange resins for the selective adsorption of ions of the heavy metals (e.g. Fe^{2+}).[26,117] The reactions of polymers containing chelating groups[26] can be successfully used to convert the soluble and fusible polymers into insoluble, infusible, heat-resistant products.

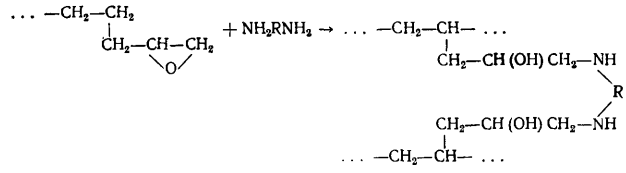
Cross-linking reactions of macromolecules due to polycondensation or migration polymerisation can be effected also with hydroxyl-containing polymers by their reaction with multivalent-metal oxides, dibasic acids, diisocyanates, and di- or poly-epoxy compounds. Such processes are widely used in the technology of protective coatings, adhesives, and plastics.

Instead of the hydroxyl-containing products of the partial hydrolysis of polyvinyl acetate or acetals, copolymers of various monomers (acrylates, methacrylates, vinyl acetate, etc.) with glycol monoesters of acrylic or methacrylic acid have been suggested[118] for the preparation of protective coatings which can be hardened by heat or chemical treatment. Equally great possibilities arise with polymers containing amino groups and in particular with polyvinylamines[119]. An example of three-dimensional copolymerisation of polyamines of high molecular weight is the reaction with alkyl or aryl diisocyanates, which usually occurs at moderate temperatures (20°–80°):

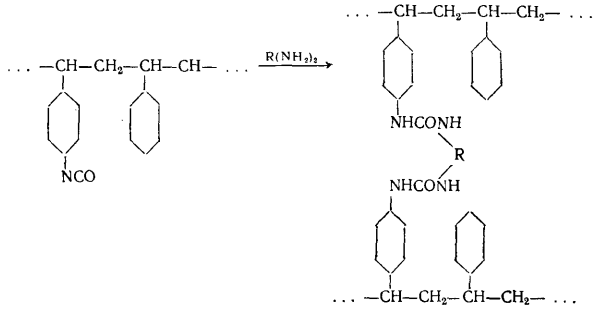


A polymer having oxygen-containing three-membered heterocycles in its side chains forms infusible and insoluble products, with high adhesion to metals and glass, by reaction with organic diamines, dibasic acids, glycols, and poly-

condensates containing amino groups (urea- and melamine--formaldehyde resins[108]):



Interesting cross-linked and branched polymers can be prepared from products of the polymerisation of *m*- and *p*-formyl, amino-,[121] and hydroxy-styrene[122,123], as well as of *m*- and *p*-styrene isocyanates[124]. These monomers, in the presence of peroxide initiators in an inert atmosphere at 110°–120°, are able to form copolymers with styrene and acrylates. The side chains of such copolymers contain some hydroxyphenyl, formylphenyl, or phenyl isocyanate groups which can undergo various reactions leading to the formation of network polymers. Thus copolymers containing 10–15 parts by weight of *p*-formylstyrene or styrene isocyanate and 85–90 of styrene can be instantaneously hardened by the addition of very small amounts of diamines:



Analogous copolymers of *m*- or *p*-hydroxystyrene at elevated temperatures react vigorously with hydroxymethyl derivatives of phenol and urea to form strong, heat-resistant plastics with good electrical insulating properties.

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CATALYTIC SYNTHESIS OF ALKYLPHENOLS

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INTRODUCTION

The chemistry of phenols has developed rapidly during the last two decades. One of the lines of work in this field has been the synthesis of alkyl derivatives, the investigation of their properties, and the search for methods of effective application of the alkylphenols in industry.

Among the most important uses of alkylphenols, their application, due to their easy oxidisability, as antioxidants for aviation fuels[1-5], lubricants[6-9], various fats[10-13], natural rubber, synthetic rubber[13-17], and other organic compounds[18-23], is of interest. Alkylphenols are also used as depressors for lubricants[24-27], as starting materials for the preparation of herbicides and fungicides[28], bactericides[29], insecticides[30] and as disinfectants[31]. This list of examples of the practical application of the alkylphenols shows the wide prospects for their utilisation in the national economy.

In the present article an attempt is made to give a survey of the numerous investigations on the catalytic synthesis of alkylphenols, which possesses a number of advantages over other methods by virtue of the simplicity of the starting materials, the accessibility of catalysts, and the high yields of alkylated products.

Since the most frequently used starting materials are unsaturated hydrocarbons, alcohols and alkyl halides, it is useful to systematise the literature according to the nature of the phenolic substances being alkylated. In the individual sections, the subject is considered in relation to the catalysts, the nature of which to a considerable extent determines the structures and relationships of the alkylated products.

The catalysts are usually various acid agents: sulphuric, phosphoric, boric, hydrohalogenic, and perchloric acids, boron fluoride and its molecular compounds, zinc and aluminium chlorides, natural clays and industrial aluminium silicates, ion-exchange resins, aluminium phenoxide, etc.

I. ALKYLATION OF PHENOLS BY UNSATURATED HYDROCARBONS

1. The Use of Acids as Alkylation Catalysts

One of the first catalysts to find application in the alkylation of phenols by alkenes was sulphuric acid[32-34], which has been used in this reaction not only as such, but also in mixtures with other substances — acetic[32-37] and boric[38] acids, and also with salts, for example ammonium sulphate[39].

The quantity of sulphuric acid used has varied a lot. Thus, Koenings[32-34] used for the alkylation of phenols by isopentene and styrene ten volumes of a solution of 1 part of concentrated sulphuric acid in 9 parts of glacial acetic acid. However, in subsequent work, the quantity of sulphuric acid was considerably diminished, and at the present time it amounts to 3–10% of the weight of phenol[40-44].

Mamedaliev[42] investigated the influence of the quantity of sulphuric acid on the yield in the alkylation of *o*-cresol by alkenes. It was shown that the use of above 5% of the acid led to a reduction of the yield, particularly that of monoalkylated products.

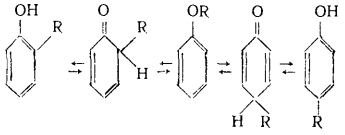
In the literature there is no mention of the preparation of ethylphenols by the alkylation of phenol by ethylene in

the presence of sulphuric acid. It was not until 1958 that Mamedaliev[42] carried out such an alkylation of *o*-cresol, but the ethyl-*o*-cresols were not isolated. Under the same conditions (140°–150°), alkylation of *o*-cresol by propene, n-butene, and isobutene gave monoalkylcresols in yields of 42, 51, and 55% respectively, and dialkyl-*o*-cresols in yields of 14, 15, and 17%.

As the alkenes of high molecular weight, and particularly those with a branched carbon chain, enter more easily into the alkylation reaction, and the products formed find a diversity of applications, the alkylation of phenols by butenes, pentenes, diisobutenes, etc. has been investigated in more detail. The temperature conditions for this reaction are very varied. In early papers[32-34] alkylation at room temperature is described; several days are required to complete the reaction and low yields of alkylphenols are obtained, the formation of the corresponding phenolic ethers being apparently favoured by the low temperature. In a series of later papers[45,46] it has been found that lowering of the temperature facilitates alkylation on the oxygen according to the following scheme[45]:

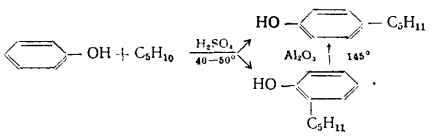
$$CH_3CH_2CH{=}CHCH_3 + H_2SO_4 \rightarrow CH_3CH_2CH_2CHOSO_3H \xrightarrow{HOC_6H_4CH_3}$$
$$\rightarrow CH_3CH_2CH_2CHOC_6H_4CH_3 + H_2SO_4.$$

Natelson[46] showed that the equilibrium phenolic ether ⇌ ⇌ alkylphenol set up in any alkylation process is displaced towards the formation of alkylphenol by a rise of temperature. Alkylation of phenol by an unsaturated hydrocarbon in the presence of sulphuric acid was begun at 0°–10°, and on raising the temperature to 65°, alkylphenols in yields up to 90% were obtained; the author considered that the increase in temperature isomerised the alkyl phenyl ether through a series of stages:



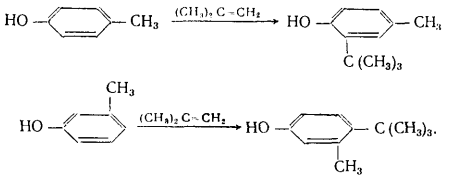
For this reason, for the direct formation of butyl- and pentyl-phenols a higher alkylation temperature is used, i.e. 40°–150°.[36,47-49]

The proportions of phenol to alkene depend on the nature of the desired product. With equimolar proportions of the original substances, the reaction results, usually, in the formation of the monoalkylphenol[44,48,50-54]. In the presence of an excess of alkene, di- and tri-alkylphenols are produced[40,47,54,55]. The orientation of the alkyl group is determined by the structure of the initial phenol and the temperature of the alkylation, as well as by the nature of the particular catalysts used. Thus, in the alkylation of phenol and of *o*-cresol by pentene at 40°–50°, a mixture of *o*- and *p*-isomers is formed[56,57], which, after prolonged treatment at a higher temperature (145°) in the presence of activated clay, gives the pure *p*-isomer[57]:

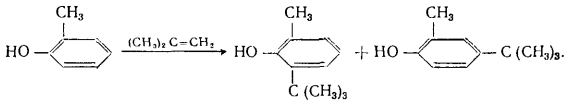


The formation of a mixture of *o*- and *p*-butylphenols is also observed in the alkylation of phenol by isobutene at 90°.[43] At a higher temperature (120°–150°) this reaction yields *p*-alkylphenol[58]. The nature and quantity of the isomers formed is also determined by the structure of the initial phenol[59,60].

Weinrich[59] investigated the structure of the isomers formed by the alkylation of cresols and xylenols by isobutene at 60°–70°. In this, *p*- and *m*-cresols form one monosubstituted t-butylcresol each, 4-methyl-2-t-butylphenol and 3-methyl-4-t-butylphenol, respectively:

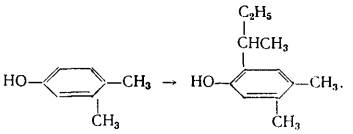


Under these conditions, *o*-cresol forms two monosubstituted products: 2-methyl-6-t-butylphenol and 2-methyl-4-t-butylphenol:



Stevens[61] accomplished a separation of isomeric cresols and xylenols by using the different solubilities, in alkali and in Claisen's solution, of the alkylphenols formed by the alkylation of the cresols and xylenols by isobutene in the presence of small quantities of sulphuric acid (3–5%). The author established a series of rules determining the position occupied by the tertiary butyl group. It was shown that the tertiary butyl group does not enter the ring between two methyl groups or between a methyl and a hydroxyl group; thus, 3,5-xylenol does not react with isobutene[61].

A characteristic peculiarity of the alkylation of phenols by alkenes in the presence of sulphuric acid is the tendency of the entering alkyl groups to isomerise in the following way: primary → secondary → tertiary. This isomerisation leads to a displacement of hydrogen atoms without alteration of the carbon skeleton. Thus, Albert[54], from the alkylation of 3,4-dimethylphenol by 1-butene, obtained 3,4-dimethyl-6-s-butylphenol:



Parker and Goldblatt[62] prepared 4-t-butylphenol from isobutene and phenol and also 4-t-pentylphenol by the alkylation of phenol by 2-methylbut-1-ene and by 2-methylbut-2-ene. Similar rules have been noted by the authors of a number of papers[33,40,42,43,45,58-60,63,64].

Ipat'ev, Pines, and Schmerling[65,66] established that the sulphuric acid isomerises alkenes in almost all cases when they are used for the synthesis of alkylbenzenes. The authors consider that the primary product of the reaction is a monoalkyl sulphate which, according to the conditions, can isomerise at a rate which depends on the structure of

the initial alkene. For example:

$$(CH_3)_2CHCH=CH_2 + H_2SO_4 \rightleftarrows (CH_3)_2\underset{\displaystyle SO_3H}{\overset{|}{C}}HCH_2CH_3,$$

$$(CH_3)_2\underset{\displaystyle SO_3H}{\overset{|}{C}}CH_2CH_3 \rightleftarrows [(CH_3)_2C=CHCH_3] + H_2SO_4.$$

The sulphate formed may subsequently give carbonium ions:

$$(CH_3)_2\underset{\displaystyle SO_3H}{\overset{|}{C}}CH_2CH_3 \rightleftarrows (CH_3)_2\overset{+}{C}CH_2CH_3 + (SO_3H)^-.$$

When the rate of the isomerisation is low (for example in the case of 1-pentene) a mixture of alkylbenzenes is formed. However, in the case of isopentene the rate of the isomerisation is sufficiently high for the formation of only t-pentylbenzene. Apparently the above scheme of the alkylation of benzene applies also in the alkylation of phenols by alkenes. The phenomenon of the isomerisation of the entering radical is observed also in the alkylation of phenols by mixed isobutene dimers, 2,4,4-trimethylpent--1-ene and 2,4,4-trimethylpent-2-ene. Niederl[67] has shown that the reaction of diisobutene with phenol (temp. 10°–50°, 5% sulphuric acid) yields the *p*-isomer, i.e. 2-(*p*-hydroxyphenyl)-2,4,4-trimethylpentane, or *p*-t-octylphenol:

$$HO-C_6H_4- + \begin{cases} (CH_3)_3CCH_2\overset{CH_3}{\overset{|}{C}}=CH_2 \\ (CH_3)_3CCH=\overset{CH_3}{\overset{|}{C}}CH_3 \end{cases} \rightarrow HO-C_6H_4-\overset{CH_3}{\overset{|}{C}}-CH_2-\overset{CH_3}{\overset{|}{C}}-CH_3.$$

In spite of the low reaction temperature, the author[67] did not succeed in isolating the t-octyl ether of the phenol, in agreement with Ipatieff's results[68]. The latter established that *p*-t-octylphenol appears as the product of this reaction only when a low temperature and small quantities of sulphuric acid are used. At a higher temperature (85°) and in the presence of large quantities (~ 20%) of sulphuric acid, *p*-t-butylphenol is obtained, for the formation of which Ipatieff suggests the following scheme:

$$CH_3CCH_2C-C_6H_4OH \begin{cases} \rightarrow p\text{-}(CH_3)_3C-C_6H_4OH \\ \rightarrow 2,4\text{-di}(t\text{-}C_4H_9)\,C_6H_3OH. \end{cases}$$

The correctness of this scheme was confirmed by the formation of *p*-t-butylphenol and 2,4-di-t-butylphenol by heating *p*-t-octylphenol with phosphoric acid to 140° in a sealed tube. Under conditions similar to those described by Niederl and other authors[69-71], *p*-t-octylphenol was prepared. The corresponding *p*-octyl substituted derivatives of the cresols[71,72] and of the dihydric phenols[71,73] were prepared under analogous conditions.

In addition to acyclic hydrocarbons, terpenes[74] and aromatic hydrocarbons with an unsaturated side chain, e.g. styrene[32,75-77] and 1-phenylprop-1-ene[78] have been used for the alkylation of phenols in the presence of sulphuric acid. Frisch[76] condensed phenol with styrene in the presence of small quantities of sulphuric acid (~1%). To be successful, this reaction requires a sufficiently high temperature (120°–200°) and a large excess of the original phenol (phenol : styrene = 4 : 1 [76] and 7 : 1.5 [77]), which decreases the polymerisation of the styrene to a minimum.

In this way, the total yield of substituted phenols reaches 75–85%; [76] the product consists of a mixture of *o*- and *p*-(α-phenylethyl)-phenols in the molar ratio 3 : 2:

$$HO-C_6H_4- + C_6H_5CH=CH_2 \rightarrow HO-C_6H_4-\underset{\displaystyle CH_3}{\overset{|}{C}}HC_6H_5 + HO-C_6H_4-\underset{\displaystyle CH_3CHC_6H_5}{\overset{|}{}}.$$

High yields of α-phenylethylphenols of the order of 85–90% were obtained by Buu-Hoï[79] by the alkylation of phenol and also *o*- and *p*-cresols by means of styrene. The reaction was carried out at 100°; a reduction in the degree of polymerisation was achieved by the dilution of the reaction mixture with toluene, thus avoiding the use of a large excess of phenols.

Niederl[78] reacted α-phenylpropene and the isomeric cresols. The reaction gave the corresponding 1-phenyl--2-hydroxy(methylhydroxyphenyl)propanes, e.g. with *o*-cresol 1-phenyl-2-(4-hydroxy-3-methylphenyl)propane was obtained:

$$C_6H_5CH=CHCH_3 + \underset{\displaystyle CH_3}{\overset{CH_3OH}{\overset{|}{C_6H_3}}} \rightarrow HO-\underset{\displaystyle CH_3}{\overset{|}{C_6H_3}}-\underset{\displaystyle CH_3}{\overset{|}{C}}HCH_2C_6H_5.$$

Apart from numerous alkenylbenzenes, 2-phenylbut-2-ene and 2-phenylpent-2-ene have been used in this reaction under the conditions described[80].

Certain sulphonic acids have been suggested as catalysts in the alkylation of phenols by alkenes. Proell[81] used C_1-C_3 alkylsulphonic acids in this reaction. These catalysts can promote the polymerisation of the original alkene at a temperature of the order of 70°. The author prepared octylphenol in 98% yield, dodecylphenol (68%) and pentadecylphenol (78%), using a catalyst of 91% RSO_3H + + 3% H_2SO_4 + 6% H_2O and the individual alkenes or their polymers as alkylating agents.

Wuyts patented the use of *p*-toluenesulphonic acid as catalyst in the synthesis of limonylphenol[82]. Kitchen[83] used benzenesulphonic acid for the synthesis of terpenylphenols. He obtained 2,4-dimethyl-6-isobornylphenol (35%) by the reaction of camphene with 2,4-dimethylphenol in toluene solution at 129°–130°. In certain cases, the sulphonic acid derivative of the phenol to be alkylated may serve as catalyst. For example, equimolar quantities of the cresol fraction and sulphuric acid were mixed; to the cresol sulphonic acid formed a fresh portion of the cresol fraction was added, the water evolved in the reaction was boiled off at 120°, and the butene dimer was added. The yield of octylcresols amounted to 86% [72,84].

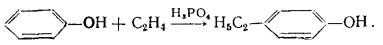
In the patent literature the use of fluorosulphonic acid in the alkylation of phenol by isobutene and diisobutene is mentioned[85]. On carrying out the reaction between phenol and isobutene in benzene solution at 25° in the presence of fluorosulphonic acid, *p*-t-butylphenol is formed almost exclusively in 84% yield with only 2.5% of the corresponding *o*-isomer; the action of this catalyst is thus essentially different from that of sulphuric acid under the same conditions[56,57].

In recent years, alkylphenols have been prepared in high yields by the use of cation-exchange resins of the sulphonated-polymer type as catalysts[86-88]. Thus, Loev[86] prepared nonylphenol, *p*-t-octylphenol and *p*-t-butylphenol in yields of 90, 73, and 88% respectively, by the alkylation of phenol in the presence of Amberlite by 1-nonene, diiso-

butene, and isobutene at 100°–110° at atmospheric pressure. Boisselet and Parc[88] used sulphonated polystyrene resins as catalysts. They prepared 2-t-butyl-*p*-cresol in 62% yield.

Isagulyants[89] used the KU-1 cation-exchange resin (a sulphonated phenol-formaldehyde polymer) and KU-2 resin (a sulphonated copolymer of styrene and butadiene) in the alkylation of phenols. At a reaction temperature of 90°–140° he obtained high yields (75–99%) of *p*-alkylphenols by the alkylation of phenol by isobutene, isopentenes, octene, styrene, etc. It is interesting to note that this author did not isolate polyalkylated products, the formation of which has been reported by workers who had used cation-exchange resins[88].

Phosphoric acid has been used much less than sulphuric acid as catalyst in the alkylation of phenols by unsaturated hydrocarbons. To a considerable extent this is explained by the greater accessibility of the latter, and sometimes also by the lesser effectiveness of phosphoric acid in the reaction[68,79]. Ipat'ev[90] succeeded in preparing ethylphenol in a yield of 43% by the alkylation of phenol with ethylene in the presence of phosphoric acid in the autoclave at 225° and a pressure of 80–95 atm. As phenetole does not isomerise under these circumstances, the reaction does not go via the formation of the ether, but takes place by direct alkylation of the nucleus:



Together with Pines and Komarevskii, Ipat'ev[90] carried out the alkylation of phenol by propene under normal and increased pressures. In both cases isopropylphenol was isolated.

Isagulyants similarly prepared isopropyl-t-butylcresols and the corresponding ethers by the alkylation of *m*- and *p*-cresols with propene and isobutene[91]. The alkylation of cresols[92,93], guaiacol[94], and dihydric phenols[95,96] by alkenes in the presence of phosphoric acid has been described.

In the literature the use of mixed catalysts for alkylation is mentioned, for example oxides or acids derived from boron mixed with organic dibasic acids or their alkyl esters[97].

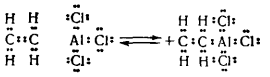
Apart from the acids mentioned above, certain halogen compounds, chiefly the hydrogen halides, are used as catalysts in alkylation. Thus, Stoermer[98] reacted styrene with phenol in the presence of hydriodic acid. The chief product was *p*-hydroxydiphenylethane with an insignificant admixture of the *o*-isomer; this is apparently connected with the greater stability of the *p*-isomer under these conditions. It was shown that under these conditions the *o*-isomer is transformed into the *p*-isomer. Calcott[99] alkylated *m*-cresol with propene in the presence of hydrofluoric acid. In spite of the low temperature at which the reaction was carried out (0°–20°), he separated monoisopropyl-*m*-cresol. In the presence of the same catalyst, s-hexylresorcinol and s-hexyl-α-naphthol were prepared from 3-hexene and the corresponding phenols in yields of 45–57%.[100] A number of patents[101–105] describe the use of hydrogen halides in the alkylation of phenols by alkenes.

In the literature there are scattered references to the use of other halogen compounds in this reaction — in particular perchloric acid[104], its salts[105–106], and phosphorus oxychloride[107,108]. Thus, in the presence of a mixture of the perchlorates of aluminium and iron, or of lead perchlorate, *o*-cresol is alkylated by octene and decene with the formation of 4-s-octyl- and 4-s-decyl-*o*-cresols respectively[106]. Thus, a catalyst of this type favours the preparation of mainly *p*-isomers.

The use of phosphorus oxychloride[107,108] in the alkylation of phenol by isobutene makes it possible to obtain the *o*-isomer in considerably greater quantity than the *p*-isomer. It has been established that the temperature exerts an insignificant influence on the ratio of the isomers[107].

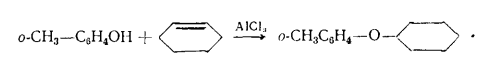
2. Catalytic Action of Metal Chlorides in the Alkylation of Phenols by Alkenes

It has been found that aluminium chloride can be used without activators in the alkylation of phenols by alkenes, giving high yields of alkylphenols. The mode of action of the aluminium chloride in this case, as of other catalysts with an electron deficit in the molecule, leads to the formation of an activated complex with the alkenes:



This complex interacts with the electron pair of the aromatic nucleus, after which the catalyst is eliminated[109].

As in the use of sulphuric acid, the reaction is accompanied by the isomerisation of the radical, and also by its rupture, for example on introduction of the t-octyl radical into the nucleus. Smith[110], by the alkylation of phenol with diisobutene in the presence of aluminium chloride obtained a 67% yield of t-butylphenol and only 14% t-octylphenol. A side reaction in the alkylation with alkenes in the presence of aluminium chloride is the formation of chloro derivatives[111], by the addition of hydrogen chloride to the initial alkene, which the low temperature favours[112]. The formation of alkylphenyl ether or of alkylphenols in the alkylation of phenols by alkenes in the presence of aluminium chloride is determined by the reaction temperature. Nortz[111] carried out the reaction between *o*-cresol and cyclohexene at 30° and obtained the corresponding cyclohexyl ether:



Levas[112] suggested two different ways of carrying out this reaction to yield as the final product the alkoxybenzene or the alkylphenols: (1) formation of the ether by carrying out the reaction in carbon disulphide at 0° and (2) synthesis of the alkylphenols at 100° without a solvent. In this reaction cyclohexene and other cyclic unsaturated hydrocarbons have been used, for example, terpenes[113]. Thus, from 2,4-dialkylphenols, 2,4-dimethyl-6-isobornylphenol and 2,4-di-s-butyl-6-isobornylphenol were prepared. The size of the alkyl groups in the starting phenol is limited to five carbon atoms on account of steric hindrance.

In recent years, aluminium chloride has come into use in this reaction in the form of a compound with sulphuric acid, to which authors give the formula $AlCl_2 . HSO_4$.[114] The preparation of detergents based on alkylphenols with a long chain of carbon atoms, synthesised in the presence of this catalyst, by the alkylation of phenol at 80° with alkene polymers containing from 16 to 30 carbon atoms has

been described[114]. In certain cases, a little boric acid is added to the aluminium chloride[115].

Zinc chloride has also been used as catalyst for the alkylation of phenols by alkenes. A series of patents[116-119] describe the use of zinc oxide and gaseous hydrogen chloride for this purpose.

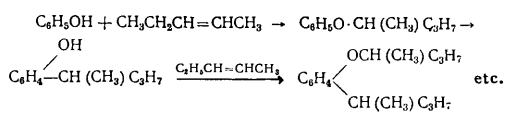
Shuikin and coworkers[120] used a mixed catalyst of zinc chloride and aluminium oxide for the alkylation of the isomeric cresols by pentenes. The reaction was carried out at 150° and 2–3 atm, and in all cases was accompanied by the isomerisation of the initial alkene; the final product of alkylation of the cresols by normal pentenes was s-pentylcresol and that in the alkylation by isopentenes consisted of t-pentylcresols, mainly the *o*-isomers[63,120].

The literature refers to the use in this reaction of ferric chloride[113,121] and stannic chloride[113,122]. Aluminium silicates have also been used in the production of alkylphenols. The reaction is carried out by mixing the initial phenol, alkene, and an inert diluent (cyclohexane or low-boiling paraffin), and passing the mixture over the catalyst at 90°–200° under 6–60 atm pressure[123]. In certain cases the catalyst is placed in a vertical tube into the bottom of which the alkene (isobutene) is let in, and the phenol is added from above. In this way, at 127° and 15 atm, 2,4-di-t-butylphenol (yield 48%) and other alkylphenols were obtained[124]. Where a higher-boiling alkene (diisobutene) was used, the reaction with the aluminium silicate catalyst is carried out at atmospheric pressure[125]. The use of activated silicates as alkylation catalysts is also described in other American patents[126-128].

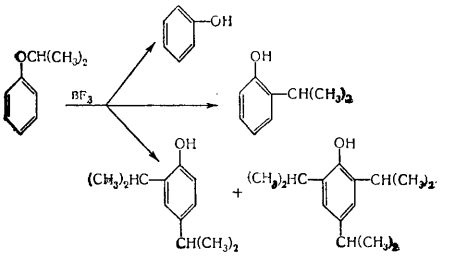
3. Boron Fluoride as Catalyst for the Alkylation of Phenols by Alkenes

During recent years boron fluoride has become widely used as an alkylation catalyst, and various other catalysts based on it have been prepared*.

A series of molecular compounds of boron fluoride, $(C_2H_5)_2O.BF_3$, $H_3PO_4.BF_3$, $BF_3.H_2O$, etc.[130-132] are used as catalysts in the alkylation of phenols by alkenes. Boron fluoride as a catalyst possesses one clearly marked peculiarity, namely the power of polymerising alkenes at a relatively low temperature. Thus in its presence propene polymerises to products above the trimer even at ordinary temperature. Therefore, in the utilisation of boron fluoride for the alkylation of phenols, careful choice of the catalyst concentration, temperature, and time of contact is required. As in the use of other catalysts, in working with boron fluoride either alkylphenols or the phenolic ethers may be formed. Sova[133] obtained a mixture of *o*-isopropylphenol and phenyl isopropyl ether on alkylation of phenol by propene in the presence of boron fluoride at -2°. Zavgorodnii[134] showed that the reaction of phenol with 2-butene between -10° and -5° gives s-butylphenol, which amounts only to one-third of the total quantity of the reaction products formed in a yield of 81%. At room temperature the total yield reaches 90%, through an increase of the quantity of alkylphenols in the catalysate. On further increase of temperature to 53° monoalkyl derivatives of s-butyl phenyl ether are formed. The reaction of phenol with 2-pentene goes similarly[135]:



As in the alkylation of phenols by alkenes in the presence of sulphuric acid, it seems that in alkylation with boron fluoride the reaction goes through the formation of a phenolic ether which subsequently isomerises to a second intermediate possessing a quinonoid structure[136]. Such an isomerisation in the presence of boron fluoride is accompanied by the formation of the phenol and also of the di- and tri-substituted phenols and the corresponding ethers[137], which considerably complicates the separation of the alkylation products:



In the patent literature[138] it is stated that the use of $BF_3-H_3PO_4$ makes possible the preparation of monoalkyl phenols. The use of a large excess of phenol (2–6 moles per mole of alkene) in the presence of this catalyst gave *p*-t-butylphenol in 80% yield. By a similar method *p*-isopropylphenol, t-butyl-*m*-cresol and cyclohexylphenol were prepared.

Another peculiarity of the boron fluoride-phosphoric acid catalyst is its power of directing the entering alkyl group to the *p*-position, while in the majority of cases, when boron fluoride is used, the *o*-isomer preponderates in the alkylation products[133,139]. The alkylation of phenols by alkenes in the presence of boron fluoride is described in a series of patents. The temperature recommended for this reaction varies within wide limits from 25°[140] to 100°[141-143], and the quantity of catalyst amounts to 0.1–1.5 wt.% of the phenol taken[143-145].

In view of the possibility of the polymerisation of the alkenes by boron fluoride, the alkylation of phenols by alkenes is sometimes carried out by first polymerising the alkene and allowing the polymer to alkylate the phenol. This gives the possibility of preparing alkylphenols with long side chains; these find wide application for the preparation of emulsifiers and detergents[146-150]. However, in those cases where polymerisation of the initial alkene is not desired, a large excess of phenol (1 : 6) must be used[138].

High yields of alkylphenol can be obtained by the use of boron fluoride etherate as catalyst. Topchiev and coworkers[130,151] prepared alkylphenols in this way in almost quantitative yields, mostly *p*-substituted. Thus, the molecular compound of ether and boron fluoride produces the same orientation of the substituent as does the molecular compound of boron fluoride and phosphoric acid[138]. Apart from open-chain alkenes, cyclic olefines have also been used in the synthesis of alkylphenols in the presence of boron fluoride. Lefebvre and Levas[152] investigated in detail the reaction of cyclohexene and phenol in the presence of boron fluoride. On carrying out the reaction at 0°, phenoxycyclohexane was obtained in a yield of 61%, with

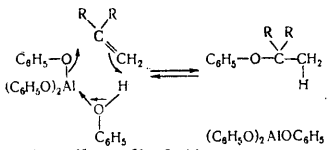
* For the properties of boron fluoride and its application in alkylation, see Topchiev et al.[129].

only 14% of cyclohexylphenol, of which 80% was the *o*-isomer and 20% the *p*-isomer. Under other conditions, at 19°–36° in carbon disulphide, the yield of cyclohexylphenols reached 57% (76% of *p*-isomer and 24% of *o*-isomer)[153]. The di- and tri-alkyl derivatives, together with the monoalkyl derivatives, were formed[154]. From *o*-cresol, under the same conditions, 2-methyl-4-cyclohexyl and 2-methyl-6-cyclohexylphenols were prepared in a yield of 54%, together with 41% of *o*-methylphenoxycyclohexane[155]. Besides cyclohexene, certain terpenes have been used in this reaction: menthene[156], dipentene*[157], terpinolene[113,157], pinene and limonene*[158].

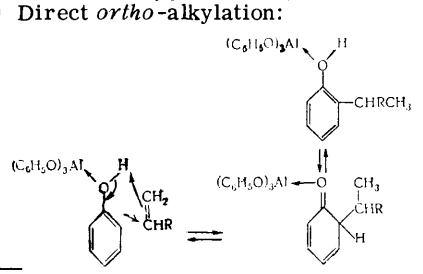
Apart from the acid catalysts described above, certain metallic salts and oxides are employed in the alkylation reaction. Thus, by alkylating phenol with ethylene in the presence of basic aluminium phosphate at 280°–400° and 40–100 atm, Semerano[159] prepared ethyl- and diethyl-phenols. Under approximately the same conditions, Shaad prepared *o*-isopropylphenol[160] using calcium hydrogen phosphate as catalyst. In the literature there is a mention of the use of other salts — molybdates of copper, nickel, and cobalt[161].

Particular interest attaches to the use of aluminium phenoxide as catalyst for the alkylation of phenols by alkenes to prepare the inaccessible *o*-substituted alkylphenols. This has been described in a series of papers in recent years. As is well known, the *p*-derivative usually preponderates in alkylation reactions; consequently, if the *p*-position is not blocked the 2,6-dialkylphenols are not formed and their synthesis must be brought about indirectly. The use of this catalyst in the synthesis of a series of *o*-alkyl- and *o,o'*-dialkyl-phenols by the alkylation of phenol with alkenes has been described by Kolka[162,163]. As in other cases, the nature of the final product depends on the temperature: at a relatively low temperature the phenolic ether is formed, while at a higher temperature the *p*-isomer is obtained; thus, aluminium phenoxide can serve for the *ortho*-alkylation only within a definite temperature range. Kolka established that the reactivity of the alkenes falls in the series $R_2C=CH_2 > RCH=CH_2$ or $RCH=CHR > CH_2=CH_2$, which is typical of reactions involving the formation of a carbonium ion. As is known, aluminium alcoholates form coordination compounds with the alcohol, and although acids of the type $HAl(OR)_4$ have not been isolated, some authors[162,163] postulate their existence and suggest the following mechanism for this reaction.

(*a*) Ether formation:

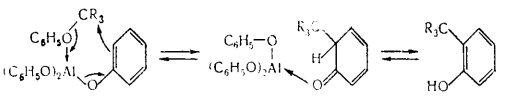


(*b*) Direct *ortho*-alkylation:



* Dipentene and limonene are the same compound (Ed. of Translation).

(*c*) *Ortho*-alkylation through the ether:



Under the optimal conditions found for each case, the corresponding 2-alkyl- and 2,6-dialkyl-derivatives were prepared in high yields: 2,6-di-s-butylphenol (74%), 2-cyclohexylphenol (42%), 2-(dec-2-yl)phenol (49%), 2,6-diisopropylphenol (61%), 2-ethyl-6-s-butylphenol (58%).

Stroh[164] has obtained similar results. The preparation of a series of *o,o* -disubstituted phenols by the alkylation of phenol with ethylene, propene, isobutene, etc., in the presence of the above catalyst has been described in a U.S. patent[165]. A number of patents[166,167] have described the alkylation of phenol, ethylphenol, and cresol by alkenes in the presence of metals that form salts with the phenol (aluminium, zinc, etc.). To increase the rate of solution of aluminium in the phenol, the addition of mercuric chloride is recommended[168].

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A survey of the results in the literature on the catalytic alkylation of phenols by unsaturated hydrocarbons shows that the most widely used catalyst is sulphuric acid. The high yields of alkylphenols and the accessibility of sulphuric acid give a certain advantage compared to the other catalysts used in this reaction. If the structure of the original phenol permits, alkylation in the presence of sulphuric acid usually forms a mixture of *o*- and *p*-alkylphenols, in which a rise of temperature leads to an increase in the yield of the *p*-isomer. Apparently, alkylation in the presence of ion-exchange resins is quite promising, and leads to high yields of alkylphenol and not to rupture of highly branched alkenes (of the diisobutene type), as occurs when sulphuric acid and aluminium chloride are used. The use of boron fluoride and of a few of its molecular compounds is very interesting in those cases where the alkylation may be combined with a preliminary polymerisation of the original alkene in order to prepare alkylphenols with long side chains — initial substances in the synthesis of detergents. However, here much work is still required in the investigation of the conditions necessary for the preparation of a particular product.

For the synthesis of *o*-alkylphenols it is apparently necessary to employ aluminium phenoxide; within a definite temperature interval it is then possible to obtain high yields of *o*-alkylphenols, which are not easily accessible.

II. ALKYLATION OF PHENOLS BY ALCOHOLS*

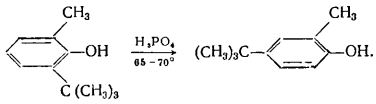
In the synthesis of alkylphenols by the catalytic alkylation of phenols with alcohols, a much smaller number of

* Apart from alcohols, the corresponding ethers or sulphonic acid esters may be used as alkylating agents[168]. It seems that the ethers, under the influence of the catalyst, break down with formation of a carbonium ion, which takes part in the electrophilic substitution reaction of the aromatic nucleus being alkylated[169]. Ethyl *p*-toluenesulphonate[170], benzyl benzenesulphonate[171] and diisopropyl sulphate[172] have been used as alkylating agents.

catalysts has been used to carry out the reaction in the liquid phase; the chief are phosphoric acid, chlorides of aluminium and zinc, and, to a less extent, sulphuric acid and boron fluoride. For alkylation in the vapour phase, aluminium oxide and natural clays are used as catalysts.

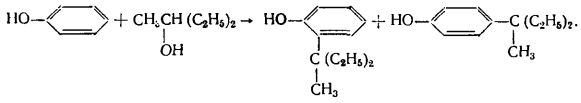
Phosphoric acid is preferred to other catalysts in the alkylation of phenols, because, by using equimolar quantities of the reacting substances, it is possible to prepare monoalkylphenols in yields up to 90%; with other catalysts, complicated mixtures of various alkylation products are formed.

Tsukervanik and Tambovtseva[173] investigated the temperature conditions for the alkylation of phenols by various alcohols in the presence of phosphoric acid. They established that the condensation goes on only at a raised temperature: tertiary alcohols react between 70° and 80°, iso-alcohols [primary and secondary iso-alcohols? (Ed. of Translation)] enter into reaction at 80°–100°, and for alkylation by normal primary alcohols the temperature required reaches 100°–130°. In the alkylation of phenols by alcohols at these temperatures, mainly the *p*-isomers are formed. The highest yields of alkylphenols are obtained in the alkylation with tertiary and secondary alcohols. Chichibabin[174] showed that among primary alcohols only benzyl alcohol reacts well. In a series of papers[174-177] he confirmed that secondary and tertiary alcohols condense with phenols at 50°–65°, forming mainly *o*-alkylphenols, with little *p*-isomer. Hart[178] later showed, by carefully investigating the products of alkylation of *m*-cresol by trimethylcarbinol under the conditions used by Chichibabin, that the tertiary butyl group enters the position *ortho* to the hydroxyl and *para* to the methyl group. However, Chichibabin's statement that he prepared 2-methyl-6-t-butylphenol by the alkylation of *o*-cresol with trimethylcarbinol is incorrect, since the substituted phenol prepared by him was easily soluble in 10% alkali, which is not the case for *o,o*-disubstituted phenols. Hart[178] synthesised 2-methyl-6-t-butylphenol by another method and it differed from the compound previously prepared by Chichibabin. Therefore, the latter substance probably consisted of the *p*-isomer formed from the corresponding *o*-isomer as a result of the isomerising influence of the temperature and phosphoric acid. This was confirmed by Hart in an experiment on the isomerisation of 2-methyl-6-t-butylphenol:

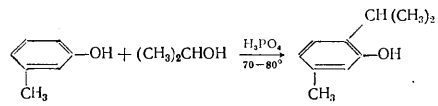


Under the same conditions, 4-t-butyl-*o*-cresol was also prepared by Dubinin[179]. Thus, as in the presence of certain other catalysts, the position taken by the radical to a large extent depends on the structure of the initial phenol and on the temperature.

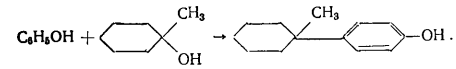
Buu-Hoï[180], in the alkylation of phenol by methyldiethyl carbinol in the presence of phosphoric acid, prepared *o*- and *p*-t-hexylphenols:



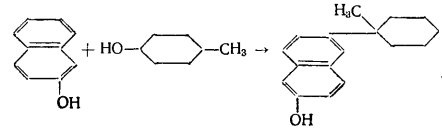
Mitsui[181] synthesised 2-methyl-4-isopropylphenol by the condensation of *o*-cresol with isopropyl alcohol. Several workers have investigated the alkylation of dihydric phenols by aliphatic alcohols in the presence of phosphoric acid. Thus, Tambovtseva[182] prepared the corresponding alkylresorcinols and alkylcatechols in yields up to 70% by the alkylation with isopropyl and n-butyl alcohols. The optimal temperature for the alkylation with isopropanol was 120°–140° and for the reaction with n-butanol it was 150°–160°. Buu-Hoï[183] prepared 4-t-pentylresorcinol, 4-t-butylguaiacol, and 4-t-butylcatechol by the alkylation of the corresponding phenols with isopentyl and isobutyl alcohols. The alkylation of *m*-cresol by isopropyl alcohol is described in the patent literature for the preparation of thymol[184]:



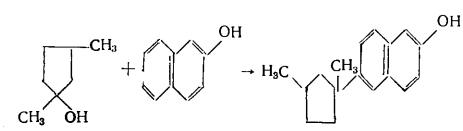
The use of cyclic alcohols in this reaction gives high yields of cyclohexylphenols. Thus, Abdurasuleva[185] prepared a mixture of *p*-cyclohexylphenols in 80% yield by the alkylation of phenol with cyclohexanol. Sidorova[186] isolated 4-(1-methylcyclohexyl)phenol from the products of the alkylation of phenol with 1-methylcyclohexanol at 100°–120°, the *o*-isomer not being found in the reaction products:



It is interesting that even at the relatively high temperature employed an ether was also formed and, in the process of distillation, was transformed into 4-(1-methylcyclohexyl)phenol, the total yield of which finally amounted to 79%. Cyclohexanol was used for the alkylation of β-naphthol[183] under the conditions suggested by Chichibabin[177]; the yield of 6-cyclohexyl-2-naphthol formed in this way was, however, very small. The authors proved the structure of this isomer by a series of reactions. It was suggested that its formation resulted from an increased electron density in positions 1 and 6 of the naphthalene[187]. The alkylation of β-naphthol by methylcyclohexanols gives good yields of the monosubstituted product, the structure of which is identical for all three isomers; for example, in the case of 4-methylcyclohexanol the reaction goes in the following way:



Thus, apparently, an isomerisation of the methylcyclohexenes formed as intermediates takes place. This phenomenon was earlier observed by Schrauth[36], who, in the alkylation of phenol by isomeric methylcyclohexanols in the presence of sulphuric acid, obtained in all cases one product, namely 4-(1-methylcyclohexyl)phenol. Buu-Hoï[188] used 1,3-dimethylcyclopentanol in this reaction and obtained 6-(1,3-dimethylcyclopentyl)-2-naphthol:



The quantity of phosphoric acid necessary for the reaction is very large. Thus, in the preparation of monoalkylphenols, 400 g of phosphoric acid are required per mole of phenol and per mole of alcohol[174,176,177]. For the introduction of two or three alkyl groups into the phenol nucleus, a correspondingly increased quantity of alcohol is used with the same quantity of phosphoric acid[189]. By the alkylation of phenol with n-butyl alcohol at 130°–150°, Sidorova[189] prepared dibutylphenol in 70% yield. The yield of the trisubstituted derivatives at this temperature is not high, apparently because under these conditions partial dealkylation takes place.

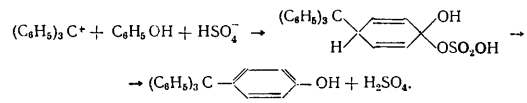
The use of sulphuric acid in the alkylation of phenols by alcohols has been described in only a few publications, mainly patents. Aliphatic alcohols*, cyclohexanol, and certain aromatic alcohols have been employed. The alkylation of phenol by aliphatic alcohols was carried out at 10°–25°[191-192], and also at higher temperatures, from 90° to 160°[193,194]. Thymol[194], *o*-s-butylphenol[195], t-butylphenol, and t-pentylphenol[196,197] were prepared from *m*-cresol, phenol, and the respective aliphatic alcohols. There is a very interesting paper by Meyer and Bernhauer[198], who investigated the alkylation of phenols by alcohols in the presence of 70% sulphuric acid. It was found that the reaction goes at 70°–80° with any aliphatic alcohol, and with benzyl alcohol, even at 40°. The authors suggest that the reaction proceeds via the formation of the corresponding unsaturated hydrocarbons with their subsequent transformation to alkylsulphonic acids, which then alkylate the aromatic nucleus. This, the authors suggest, explains the impossibility of carrying out the reaction with methyl alcohol. However, the mechanism of alkylation by benzyl alcohol and the unusual ease with which it condenses remain unclear. Deno and Chafetz[199] carried out the alkylation of hydroquinone at 0°–5° in the presence of 75–90% sulphuric acid. They isolated disubstituted hydroquinones in yields of 40–70%. In some papers it is indicated that, for increased yields, the water formed must be removed. One of the patents[200] describes the alkylation of phenols by isobutyl and isopentyl alcohols in the presence of sulphuric acid in such a way that the water formed is removed; the yield of alkylphenol exceeds 90%. The alkylation by cyclohexanol[201] proceeds similarly.

In alkylation in the presence of sulphuric acid, isomerisation of the substituting radical is always observed, which suggests that isomerisation occurs in the alkyl cation formed in the reaction between the alcohol and the sulphuric acid:

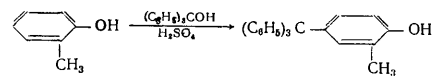
$$CH_3CH_2CH_2OH + HOSO_3H \rightarrow [CH_3\overset{H}{\overset{\vdots}{C}}HCH_2OH]^+ + (OSO_3H)^-$$
$$(OSO_3H)^- + H_2O + CH_3\overset{+}{C}HCH_3 \leftarrow CH_3CH_2CH_2^+ + H_2O + (OSO_3H)^-$$

Of the aromatic alcohols, benzyl alcohol[198,202,203] and triphenylcarbinol[204-207] have been used for the alkylation of phenols. The latter has been employed with a Baeyer's technique[205]; the reaction was carried out in the presence of a mixture of sulphuric and acetic acids. In this, the yield of, for example, 4-hydroxytetraphenylmethane reached 97%. The authors[204] suggest that the reaction goes through the intermediate formation of a carbonium ion as follows:

$$(C_6H_5)_3COH + H_2SO_4 \rightarrow (C_6H_5)_3COSO_2OH \rightleftarrows (C_6H_5)_3C^+ + SO_4H^-$$



Alkylation of *o*- and *m*-cresols under similar circumstances gives high yields (up to 80%) of the corresponding substituted tetraphenylmethane, for example:

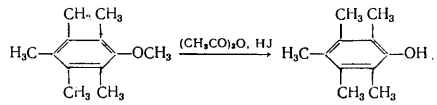


The use of anhydrous hydrogen fluoride in this reaction is very interesting. Calcott[99] described the alkylation of certain phenols in the presence of this catalyst at 2°–25°. The alkylation proceeds smoothly, without side reactions; it is always the nucleus that is alkylated and not the oxygen, because the other does not isomerise under the reaction conditions. Triisopropylphenol (94% yield), monoisopropylhydroquinone (39%), diisopropyl-2-naphthol (94%), etc. were prepared[99]. As with the alkenes, perchloric acid is sometimes used in alkylation by alcohols[208,209].

Investigations of the use of boron fluoride in the alkylation of phenols are described in only a few papers. Thus, Sowa[210] showed that neither methyl nor ethyl alcohol react with phenol in the presence of boron fluoride on heating at atmospheric pressure; they react at 170° in a sealed tube, in which the main product consists of alkyl phenyl ethers, alkylphenols being formed in only small quantity. At 115° n-propyl and isopropyl alcohols give an identical product — the isopropyl ether of *O*-isopropyl-2,4-diisopropylphenol. The authors consider that this proves that the reaction involves the intermediate formation of an alkene as follows:

$$C_nH_{2n+1}OH \rightarrow C_nH_{2n} + H_2O,$$
$$C_6H_5OH + C_nH_{2n} \rightarrow C_6H_5OC_nH_{2n+1},$$

and not the initial formation of an ether and its subsequent rearrangement. The methylation of the phenol nucleus in the presence of boron fluoride was achieved by Kolka and Vogt[211]: methyl alcohol was saturated with boron fluoride to give boron fluoride etherate, $(CH_3)_2O.BF_3$, which on boiling with phenol formed methyl ether and the *O*-methyl derivatives of the phenols. The latter are easily converted to the corresponding phenols by hydriodic acid:



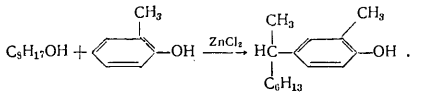
Apart from boron fluoride, the use of fluoroboric acid[212] has been described, but it possesses no advantage over sulphuric acid for alkylation with alcohols.

Metal chlorides have been used for a long time in the alkylation of phenols by alcohols. Liebmann[213,214] showed that the reaction goes very easily on short heating of the reactants at 180° in the presence of zinc chloride. Senkowski[215] later showed that the phenols prepared by Liebmann consisted of the *p*-isomers. Later still Anschütz[216] discovered that in the presence of zinc chloride an isomerisation occurs, so that the phenols prepared by Liebmann were t-alkyl derivatives. The technique suggested by

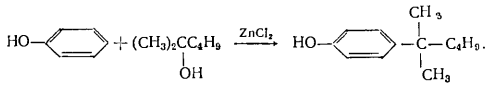
* In a Japanese patent[190], the alkylation of phenols by ethers, for example, di-n-butyl ether, in the presence of sulphuric and other acids, is described.

Liebmann was later utilised in the alkylation of phenol by n-butyl[217], s-butyl[218], t-pentyl[219], dodecyl[220], and cetyl[221] alcohols, by cyclohexanol[218], and also in the alkylation of the cresols by isobutyl alcohol[222,223] and of guaiacol by various alcohols[224].

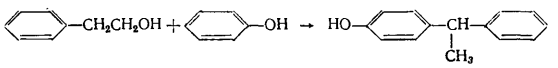
Degering[225] observed that the alkylation of phenols in the presence of zinc chloride usually occurs in the *p*-position, and when this is substituted, in the *o*-position, without the formation of *m*-isomers, in contrast to the case when aluminium chloride is used. The author carried out the alkylation of *o*-cresol by octyl, dodecyl, caprilic, and other alcohols and found that in the mixture of isomers formed the 2-methyl-4-alkylphenol predominated, for example:



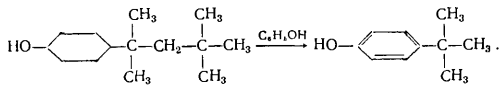
In the alkylation of *p*-cresol the corresponding *o*-alkyl-*p*-cresol is formed, the yields reaching 70%. The formation of the *p*-isomers was also observed by McGreal[80] in the alkylation of phenol by dimethylisopropylcarbinol and dimethyl-n-butylcarbinol in the presence of zinc chloride:



Diisobutyl alcohol (2,2,4-trimethylpentan-4-ol) does not form *p*-t-octylphenol with phenol under analogous conditions, the chief reaction product being *p*-t-butylphenol. The author[81] investigated the behaviour of primary, secondary, and tertiary aromatic alcohols in this reaction: phenylcarbinol, phenylmethylcarbinol, benzylcarbinol, phenylmethylethylcarbinol, and phenylmethylisopropylcarbinol. When benzylcarbinol was used, instead of the expected 4-hydroxydibenzyl, *p*-(α-phenylethyl)phenol was isolated:



The formation of such a phenol indicates that dehydration of the alcohol precedes the reaction with the phenol. In the case of the remaining carbinols the condensation went normally with the formation of the corresponding *p*-alkylphenols, the yields of which varied from 40 to 80%. Cyclic alcohols (cyclohexanol and cyclopentanol) alkylate phenol at 170°–180°, in the presence of zinc chloride, giving a mixture of *o*- and *p*-substituted phenols[226]. The isomeric methylcyclohexanols form methylcyclohexylphenol[80] in this reaction. An attempt to introduce 4-t-octylcyclohexanol into the reaction with phenol under similar conditions did not yield the desired result, as *p*-t-butylphenol was again obtained:



The alkylation of phenol by primary alcohols in the presence of zinc chloride in hydrochloric acid solution at 100°–140° has been described[227,228]. For example, *p*-t-butylphenol was thus prepared[228]. There is also mention of the use in this reaction of magnesium chloride[229]; reaction of *m*-cresol with propyl alcohol in a sealed tube at 200°–210° gave methylpropylphenol. Recently magnesium chloride has not been used, apparently on account of its greater cost and the difficulty of its regeneration.

The use of aluminium chloride in the alkylation of aromatic compounds by alcohols has been investigated in detail by Huston, Tsukervanik, and others. In the early papers the view is expressed that primary alcohols do not enter the condensation reaction in the presence of aluminium chloride, and that secondary alcohols condense with difficulty. Huston[230], for example, considered that condensation was possible only with alcohols in whose molecules the hydroxyl was activated by a double bond or a benzene ring. Later, Tsukervanik[231] showed that for the condensation of phenols with primary and secondary alcohols, different proportions of the reagents and a higher temperature were required. Huston[230] conducted his experiments at 25°–30° with molar proportions of phenol, alcohol, and aluminium chloride of 1 : 1 : 0.5. Tsukervanik[231], using a different proportion, 1 : 1 : 2*, and a higher temperature (110°–125°), obtained up to 70% of mixtures of the *o*- and *p*-isomers in the alkylation of phenol by ethyl, propyl, n-butyl, isobutyl, and isopentyl alcohols. The reaction between phenol and secondary alcohols (isopropyl, s-butyl, and s-pentyl) in the presence of aluminium chloride gave the corresponding alkylphenols (up to 52%). Together with the alkylphenols, alkyl phenyl ethers were also found as reaction products, in quantities increasing with decreasing amount of catalyst and lowering of temperature. Therefore, Tsukervanik[231] suggested that alcoholates of the primary and secondary alcohols are first formed, and later react further:

$$ROH + AlCl_3 \rightarrow ROAlCl_2 + HCl\ ,$$
$$C_6H_5OH + AlCl_3 \rightarrow C_6H_5OAlCl_2 + HCl\ ,$$
$$C_6H_5OAlCl_2 + ROAlCl_2 \xrightarrow{HCl} C_6H_5OR + AlCl_3 + AlCl_2OH,$$
$$C_6H_5OR + ROH + AlCl_3 \rightarrow RC_6H_4OR + AlCl_2(OH) + HCl.$$

In the further decomposition of the alkyl phenyl ether three possibilities may be envisaged:

$$RC_6H_4OR + HCl \rightarrow RC_6H_4OH + RCl\ , \quad (I)$$
$$RC_6H_4OR + C_6H_5OH \rightarrow 2RC_6H_4OH\ , \quad (II)$$
$$2RC_6H_4OR \rightarrow RC_6H_4OH + R_2C_6H_3OR. \quad (III)$$

The possibility of reaction (I)[233], and reactions (II) and (III)[234,235] was confirmed. Subsequently, the possibility of the formation of mixed alcoholates of aluminium was assumed by many investigators[236,237], who suggested that these compounds decompose as follows:

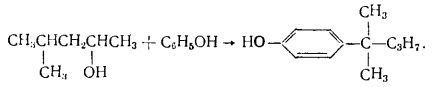
$$AlCl_2OR \rightarrow RCl + AlOCl.$$

This reaction may be utilised for the synthesis of alkyl halides. However, Tsukervanik[238] considers that a process of this nature requires a higher temperature (140°–150°), while the alkylation of phenol takes place at 90°–100°, and that at the temperature of maximum decomposition of the mixed alcoholates, the yields of alkylated products are not raised, but are actually lowered. The decomposition of the ethers thus apparently takes place through stage (II) or (III).

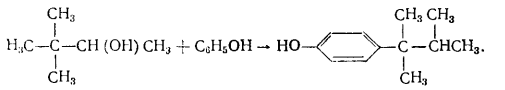
More recently, Huston[239] has achieved the condensation of phenol with more complicated secondary alcohols. The alkylation of phenol by 2-pentanol and 3-pentanol and also

* With smaller quantities of aluminium chloride, the yields did not exceed 36%.[232]

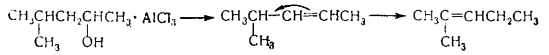
by 2-hexanol and 3-hexanol, etc. was carried out under the conditions described above[230]. The nature of the products obtained depends on the structure of the initial alcohol. Thus, the alkylation of phenol by 2-pentanol and 3-pentanol gives 2-(*p*-hydroxyphenyl)pentane and 3-(*p*-hydroxyphenyl)-pentane, and the alkylation of phenol by 2-methylpentan-4--ol gives 2-methyl-2-(*p*-hydroxyphenyl)pentane as chief product:



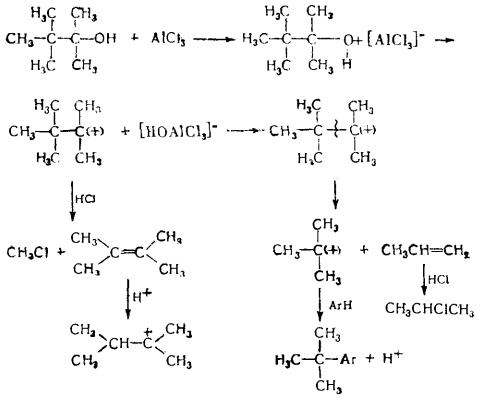
This reaction proceeds with the isomerisation of the substituting radical. Alkylation of phenol by 2,2-dimethylbutan-3-ol yields 2,3-dimethyl-2-(*p*-hydroxyphenyl)-butane:



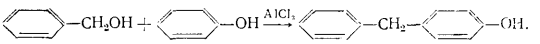
Huston and coworkers[239] suggested a mechanism for the alkylation of phenols by secondary alcohols, different from that described above. According to their ideas, aluminium chloride forms with secondary alcohols a complex that easily breaks down directly, or through the aluminate, with the formation of an alkene; this condenses with phenol in the presence of aluminium chloride. The authors consider that this explains the formation of 2-methyl-2-(*p*-hydroxyphenyl)pentane in the alkylation of phenol by 2-methylpentan-4-ol, if a migration of the double bond is supposed to precede the condensation:



The formation of 2,3-dimethyl-2-(*p*-hydroxyphenyl)-butane is explained by Huston and coworkers[239] by the appearance of an unstable carbonium ion $(CH_3)_3C-\overset{+}{C}HCH_3$, which rearranges to a more stable ion $CH_3\overset{+}{C}(CH_3)-CH(CH_3)_2$; this then condenses with the phenol. The alkylation of phenol by tertiary alcohols has been described in a series of other papers[240-247]; the yields of alkylphenols obtained varied from 2 to 80%. Huston[248,249] explains the low yields of *p*-t-alkylphenols and the formation of side products in the alkylation with alcohols having a branched chain, by the occurrence, during the alkylation in the presence of aluminium chloride, of side reactions. For example, the alkylation of benzene by 2,3,3-trimethylbutan-2-ol goes according to the scheme



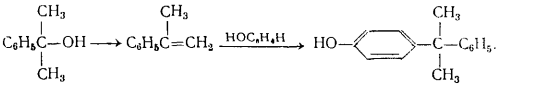
Such products have been found in the alkylation of phenols by branched-chain alcohols[245], which suggests that reactions similar to the above may also be involved. The alkylation of phenols by aromatic alcohols goes easily. Benzyl alcohol reacts with phenol in petrol ether solution at 45°–60° with the formation of up to 45% of *p*-benzylphenol[250]:



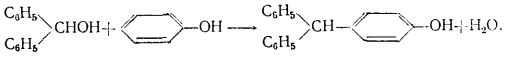
At a lower temperature (35°) the reaction hardly occurs at all. The isomeric cresols are benzylated even at 30°–35°, forming a mixture of mono- and di-substituted derivatives[251-253]. Secondary aromatic alcohols condense with phenol at temperatures of the order of 25°–40°; for example, benzohydrol gives with phenol up to 40% of *p*-hydroxytriphenylmethane:

$$(C_6H_5)_2CHOH + C_6H_5OH \rightarrow (C_6H_5)_2CHC_6H_4OH.$$

This reaction goes particularly easily with alcohols containing one or more phenyl radicals in the molecule[254-256]. With increase of the number of phenyl radicals, the yield of substituted phenols rises[255]. Thus, in the condensation of phenol with dimethylphenyl-, methyldiphenyl-, and triphenyl-carbinol the yield of *p*-substituted products amounted to 72, 80, and 95% respectively[255]. In the first two cases, an alkene was found in the reaction mixture — a product of the dehydration of the original carbinol. Welsh[255], therefore, supposes that the alkylation goes as follows:



The possibility of such a reaction mechanism when zinc chloride is used, was confirmed by McGreal[80]. In those cases where the formation of a phenylalkene is impossible, it is suggested that the water is formed from a hydrogen of the nucleus and the hydroxyl of the alcohol:



Tsukervanik and Nazarova[257] used ferric chloride in this reaction. It transpired that tertiary alcohols react with phenol and the cresols, even at room temperature, forming monoalkyl derivatives in a yield of 70–95%. The quantity of ferric chloride amounted to 0.5 g-equiv. to 1 g-equiv. of alcohol. In the alkylation by secondary alcohols 1 g-equiv. of ferric chloride was required for the same quantity of alcohol, and a temperature to 50°–60° was necessary; the yield of alkylphenols reached 38–75%. The success of this reaction with primary alcohols depends on the structure of the original alcohol. With iso-alcohols, the reaction goes at a higher temperature (120°), but normal alcohols do not condense with aromatic compounds in the presence of ferric chloride[258].

The alkylation of phenols by alcohols at a high temperature is carried out with aluminium oxide, natural clays, and aluminium silicates as catalysts. Ipat'ev and coworkers[259-261] brought about the alkylation of phenol by methyl alcohol, using aluminium oxide as catalyst at 440° and 220 atm pressure. The use of the high pressure made it possible to prepare *o*-cresol, since in the absence of

this pressure, only hexamethylbenzene is formed[262]. Ethyl alcohol gives a smaller yield[263]. Alkylation by propyl alcohol[263] was carried out at 400° and 130 atm; *o*-propylphenol was found in the alkylate, together with other alkylation products. Cullinane[264] has shown that the composition of the latter depends not only on the conditions of the reaction, but also on the nature of the catalyst used. Thus, if the reaction between methyl alcohol and phenol is carried out at 200°, mainly anisole is formed; a rise of temperature leads to the formation of *o*-, *m*-, and *p*-methylphenols, the proportions of which change with change of temperature and replacement of the aluminium oxide by aluminosilicate. Samsonova[265] investigated the reaction of phenol and methyl alcohol in the presence of a natural aluminosilicate (gumbrine) and showed that a rise of temperature to 500° makes it possible to prepare alkylphenols in a yield of up to 68%. In the alkylation of phenol by ethyl alcohol[266] the optimal temperature is 350°, at which alkylphenols were prepared in a yield of 94%. Aluminium oxide and natural aluminosilicates have been used as alkylation catalysts also in other investigations[267-274]. Aleksandrova[275] suggested a mixed catalyst consisting of thorium oxide and aluminium oxide for the alkylation of phenols by alcohols in the vapour phase. At 440° up to 60% of acidic products were prepared, constituting a mixture of alkylphenols. Hanch[276] showed later that pure aluminium oxide gives analogous results. Among other catalysts for the alkylation of phenols by alcohol in the vapour phase, a two-component silica–phosphoric acid catalyst has been successfully used[277].

A survey of research on the catalytic alkylation of phenols by alcohols thus shows that the yields of alkylphenol and their structures depend on the conditions of the reaction, among which the structure of the initial alcohol, the temperature, and the nature of the catalyst are determining factors; in some cases, the phase and pressure factor play a significant part. However, in spite of the possibility of preparing in this way alkylphenols in high yields, often reaching 90% and more, the alkylation of phenols by alcohols in industrial practice has only limited prospects, since the results of many investigators show that in the great majority of cases, the alkylation by alcohols proceeds through the formation of the corresponding alkenes. The latter are more accessible and cheaper, since they can be prepared in various processes of refining of petroleum and solid natural fuels (coal, combustible shales, peat, sapropelites). Nevertheless, the catalytic alkylation of phenols by alcohols has a number of advantages in laboratory practice and, therefore, deserves serious attention.

III. ALKYLATION OF PHENOLS BY ALKYL HALIDES

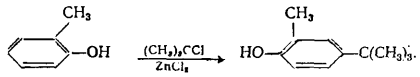
The first investigations on the alkylation of phenols by alkyl halides date back to the second half of the last century. This reaction was investigated by a number of authors, mainly using benzyl chloride. Paterno[278] and then Mazzara[279] and Rennie[280] synthesised benzylphenol by the alkylation of phenol with benzyl chloride in the presence of zinc dust:

$$C_6H_5OH + C_6H_5CH_2Cl \longrightarrow C_6H_4\begin{matrix}CH_2C_6H_5\\OH\end{matrix}.$$

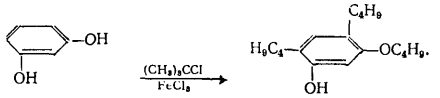
Cresol[281] and anisole[282] were employed in analogous reactions. Triphenylchloromethane also easily enters into a similar reaction, reacting with phenol in the presence of small quantities of copper* with the formation of *p*-hydroxytetraphenylmethane[283,284]:

$$(C_6H_5)_3CCl + C_6H_5OH \longrightarrow HO-C_6H_4-C(C_6H_5)_3.$$

Later the alkylation of phenols by alkyl halides was achieved mainly using zinc and aluminium chlorides, instead of zinc and copper. Zinc chloride was used by Baur[285] for the synthesis of t-butylcresols, for example:



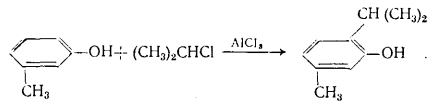
p-Hydroxytetraphenylmethane, 1-(hydroxyphenyl)-2,2,2-triphenylethane[286], and cetylphenol[287] were synthesised in a similar way. The quantity of zinc chloride used, as shown by a number of workers, may be small (0.1–0.2 mole, or even less, per mole of halide[288-290]). The quantity of zinc chloride used by Kuchkarev[288] was only 0.015–0.03 mole per mole of chloride, the zinc chloride being prepared during the reaction, from hydrochloric acid and zinc. In experiments carried out at 180°–200° Kuchkarev[288] prepared up to 70% of s-butylphenols from n-butyl chloride and phenol. An attempt to lower the temperature of alkylation to 100°–150° led to a sharp fall in the yield of alkylphenols[289]. The use of zinc chloride as catalyst in the alkylation of phenol and resorcinol by cyclohexyl chloride gives low yields of cyclohexylphenols, not exceeding 20 and 5%, respectively, of theory[291]. In the alkylation of β-naphthol by tertiary butyl chloride in the presence of zinc chloride, 6-t-butyl-2-naphthol is formed[292,293]; the formation, in this reaction, of 4-t-butyl-2-naphthol described by Contractor[294] is improbable in view of the position of the reactive sites in the naphthalene molecule and the orienting influence of the hydroxyl. In a search for a more active catalyst for the alkylation of phenols, Gurewitsch investigated this reaction in the presence of iron and aluminium chlorides[295], using tertiary alkyl halides, namely t-butyl and t-pentyl chloride and the dihydric phenols resorcinol and catechol. It was found that in the presence of ferric chloride, the ether derived from the alkylphenol is always formed too:



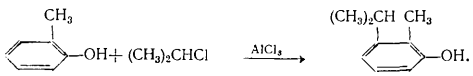
On carrying out the reaction in contact with aluminium chloride, only dibutylresorcinol is formed. Later aluminium chloride came to be fairly widely used in this reaction (described in a series of patents) and ferric chloride was employed in only a few studies[296,297]. The reason for this, apparently, is the formation of mixed products in the ferric chloride reaction, and also the low yields of monoalkylated phenols[298]. The temperature conditions vary within wide limits, according to the structure of the reactants. The alkylation of phenol itself by tertiary alkyl halides usually takes place at a low temperature (up to 50°)[299-303]; there is, however, a mention of this reaction having been carried out under more vigorous conditions (up to 200°)[301]. 4-t-Alkylphenols are usually formed, but small quantities of 2-t- and 2,4,-di-t-alkylphenols[301-304] are also obtained. The preparation of 4-t-butyl-2-naphthol by the alkylation of β-naphthol with t-butyl chloride in the presence of aluminium chloride[302] has been described, but, judging from the paper quoted above[292], formation of 6-t-butyl-2-naphthol apparently also takes place. In the

* Baeyer[283] showed that this reaction goes even in the absence of catalyst.

alkylation of phenol by t-octyl chloride in the presence of aluminium chloride, as with other alkylating agents, formation of *p*-t-butylphenol takes place[305]. Of the secondary alkyl halides, only isopropyl chloride reacts readily; with *m*-cresol (between 0° and 20°), it yields thymol[306]:

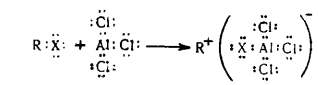


The reaction was carried out in dichloroethane solution. Under similar conditions, *o*-cresol forms 2-methyl-3-isopropylphenol[307,308]:

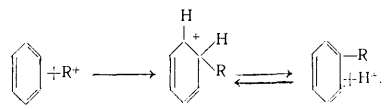


However, alkylation by other secondary and primary alkyl halides is more difficult. Tsukervanik and Tambovtseva[309] alkylated phenol with n-butyl chloride, isobutyl chloride, and isopentyl chloride by heating the mixture of the reactants to 110° in the presence of equimolar quantities* of aluminium chloride. In all cases the alkylphenols and the corresponding alkyl aryl ethers were isolated. On carrying out the reaction at a lower temperature, t-pentylphenol was obtained in a yield of 55%. Benzyl chloride[311] enters into this reaction as easily as tertiary alkyl halides. Hydroxydiphenylmethane[312] is formed in a similar way. It was found that α-halogenated ethylbenzenes react with phenols even in the absence of a catalyst with the formation of di- and tri-(α-phenylethyl)-phenols[313]. α-Phenylethyl chloride reacts with phenol on simply mixing and boiling. Hart[314] used in this reaction an optically active α-phenylethyl chloride, and showed that the alkylation products are formed directly, and not through the phenyl ethers with subsequent rearrangement. He also established that *C*-alkylation in the *p*-position is accompanied by the inversion of the configuration, but in alkylation in the *o*-position the configuration is preserved[315]. Isagulyants and Bagryantseva[316] synthesised *p*-t-butylphenol using t-butyl chloride formed directly in the reaction mixture. For this, they introduced isobutene into the reaction mixture containing phenol in the presence of aluminium chloride and a small quantity of butyl chloride, necessary for starting the reaction. Subsequently butyl chloride is formed from the isobutene and hydrogen chloride is evolved. The yield of alkylphenols reached 64%. The reaction can be carried out even in the absence of butyl chloride, by passing hydrogen chloride into the reaction mixture; in this case the yield of alkylphenols reached 71%. The quantity of catalyst only slightly influenced the yield of alkylphenols. The use of small quantities of alkyl halides as "primers" for the alkylation of phenols by unsaturated hydrocarbons is also described in other papers[317-319].

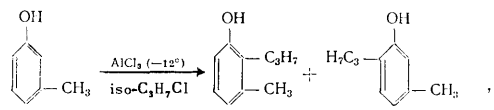
The mechanism of the alkylation of aromatic hydrocarbons by alkyl halides, which has been investigated by many workers, is apparently applicable, in principle, to the alkylation of phenols. Many authors[109,320] explain the reason for the different reactivity of alkyl halides in this reaction, carried out in the presence of aluminium chloride, as follows. It is suggested that the alkyl halide forms an ionic complex with the aluminium chloride:



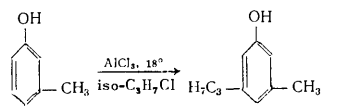
As a consequence of this, there is a weakening of the carbon–halogen bond resulting in the formation of a carbonium ion, and the alkylation itself is one case of electrophilic substitution:



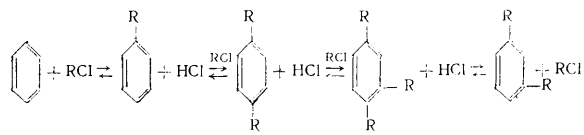
In the tertiary alkyl halides the carbon–halogen bond is extremely weak and, consequently, the formation of a carbonium ion is very probable. In recent times, Brown and coworkers[321] have suggested that the carbonium-ion mechanism cannot explain all cases of alkylation by alkyl halides. The authors regard the carbonium mechanism as applicable only in the case of tertiary alkyl halides and of other easily ionising halogen derivatives; for alkylation by primary alkyl halides they suggest a nucleophilic attack on the aromatic compound by the non-ionised complex formed as a result of reaction of the alkyl halide with aluminium chloride. Secondary alkyl halides react according to the carbonium mechanism; however, by observing special conditions and by using a medium of low dielectric constant, it is possible to achieve a nucleophilic replacement. A very interesting feature of alkylation in the presence of aluminium chloride is the anomalous orientation of the hydroxyl and methyl groups, which usually enter the *o*- and *p*-positions. Chichibabin investigated the preparation of the isomeric thymols by the alkylation of *m*-cresol with isopropyl chloride in the presence of aluminium chloride[322]. He showed that, on carrying out the reaction at -12°, *o*-thymol and 3-methyl-6-isopropylphenol were formed,



and a very insignificant quantity of *m*-thymol. However, at 18° *m*-thymol becomes the chief product of the reaction:



Chichibabin showed that *m*-thymol is the most stable isomer, since the remaining isomers are converted to *m*-thymol on heating with aluminium chloride. He also observed the formation of the *m*-isomer (3-methyl-5-butylphenol) in the alkylation of *m*-cresol by t-butyl chloride[323]. Many authors explain a similar phenomenon of abnormal replacement in the benzene nucleus by the reversibility of this reaction[321,324,325]:



* The quantity of aluminium chloride necessary for carrying out the reaction varies. Thus, according to one of the patents, the reaction was carried out in the presence of 3 wt. % of aluminium chloride[310].

The ease with which the radical replaces the hydrogen is determined by its affinity for the pair of electrons constituting its link with the benzene nucleus. The methyl group, therefore, is held more firmly than, for example, the butyl group[326]. Brown and coworkers[321], having investigated the question of orientation in the alkylation of the benzene nucleus in the presence of aluminium chloride, suggested that the place taken by the alkyl radical is determined not only by the distribution of electron density in the nucleus of the aromatic component, which depends on the substituents already present, but also by the nature of the attacking agent. The authors consider that the more reactive the carbonium ion formed (i.e. the less the relative ease of its formation), the less selectively it acts. If the carbonium ion is formed easily, its activity is more selective, and the *m*-isomer is obtained in insignificant quantity.

Apart from the catalysts mentioned above, the hydrogen halides themselves, and also boron fluoride, may be used in the synthesis of alkylphenols. The hydrogen halides have been used as catalysts only in the cases where the alkylating agent is a tertiary alkyl halide, taken as such, or arising by the action of the hydrogen halide on an unsaturated hydrocarbon. Thus, for example, there is a series of patents on the preparation of *o*- and *p*-(α-phenylalkyl)-phenols by the alkylation of phenol and catechol with 2-arylalk-1-enes in the presence of hydrogen chloride or bromide[327-329]. t-Butylphenol was obtained in a yield of 85% by the reaction of t-butyl chloride with phenol in the presence of hydrogen fluoride[330]; its yield in the presence of hydrogen chloride reached 90%[331]. But Simons[331] showed that the reaction of phenol and t-butyl chloride occurs on boiling the reactants even in the absence of a catalyst; the yield of *p*-t-butylphenol in this case amounted to 67%; t-pentylphenol was obtained in a similar way in a yield of 72%. Hart[332] considered that the alkylation of phenols by alkyl halides in the absence of a catalyst is, in fact, catalytic, the role of catalyst being played by the hydrogen halide evolved during the reaction. It was shown that in a dilute solution of *o*-dichlorobenzene at 60°, an autocatalytic alkylation of phenol and of *o*-cresol by triphenylchloromethane takes place[332]. The following reaction mechanism was suggested:

$$(C_6H_5)_3CCl \underset{\text{rapid}}{\rightleftharpoons} (C_6H_5)_3C^+ + Cl^-,$$

$$(C_6H_5)_3C^+ + \text{C}_6\text{H}_4(\text{OH})\text{H} \xrightarrow[\text{slow}]{} (C_6H_5)_3C\text{—C}_6\text{H}_3(\text{OH})\text{H}^+.$$

The first reaction is made possible by the presence of an ionising medium (for example, phenol itself). The action of the hydrogen chloride formed is similar to that of the usual acid catalyst. The authors consider that, under their conditions, there occurs a direct alkylation of the nucleus, by-passing the ether stage, inasmuch as even under such mild conditions the ether decomposes. Therefore, although the alkylation on the oxygen goes more quickly, as a consequence of its reversibility, alkylphenols will accumulate in the products. Approximately the same yield of *p*-t-butylphenol (80%) is obtained in the reaction of t-butyl chloride with phenol in the presence of boron fluoride[333]. Hart[334] made the very interesting observation that the reaction of tertiary butyl chloride with phenol is prevented by the presence in the latter of dioxane as an impurity. The authors explain this fact by the removal of the phenol from the sphere of interaction with the alkyl halide on account of the formation of hydrogen bonds with the dioxane. Tertiary butyl chloride reacts with 3-t-butylphenol at 50°–60° in the absence of a catalyst, giving 2,5-di-t-butylphenol in quantitative yield. Spectroscopic investigations showed the complete absence of the *p*-isomer[335] in the reaction products.

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Published data on the alkylation of phenols by alkyl halides show that alkylation in the presence of aluminium chloride has been most thoroughly investigated. However, it must be borne in mind that isomerisation of the radical entering the phenol molecule does not always take place [isomerisation of *O*-alkyl- to *C*-alkyl-phenol? (Ed. of Translation)]. Alkylation by tertiary alkyl halides in the presence of hydrogen halides is very convenient, particularly in cases where the alkyl halide is formed during the synthesis, which makes it possible to use the more accessible alkenes as starting materials.

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SURFACE PHENOMENA IN THE DEFORMATION AND FRACTURE OF METALS

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1

In the deformation† and fracture of solid bodies an important part is played by small quantities of surface-active substances present in the surrounding medium or forming a component of the solid itself. The basis of this phenomenon, termed the Rebinder effect, is a decrease in the free energy of the new surfaces, formed and developed in the course of deformation and fracture of the solid, owing to reversible (physical) adsorption of surface-active molecules or atoms; this facilitates the development of such new surfaces and leads to a considerable reduction in the forces required to deform and fracture the body[1-17].

Adsorption may occur in various ways: adsorbed films may be formed on the external surfaces of the body by direct approach of surface-active material from the surrounding medium, or else such films may arise on internal micro-surfaces (on the walls of micro-cracks) as a result of rapid penetration of adsorption-active atoms inside the body by surface diffusion (migration) along defects in the crystal structure — the boundaries of blocks and grains, hollow dislocation centres, etc.[4,5,11,15,16,18]. Linear and two-dimensional structural defects, having an excess of free energy, serve as points for the selective adsorption of surface-active atoms arriving from the external surface or from the bulk of the material; in consequence, the behaviour of these defects during the course of deformation of the body is changed, e.g. their mobility is altered or their growth favoured, with the formation of a large free surface[15,19].

These changes in mechanical properties under the influence of adsorption have nothing to do with corrosion processes (including intercrystalline corrosion in polycrystalline solids), since they are produced by chemically inert media or by impurities present in extremely small amounts[5,11]; nor are these effects connected with dissolution, since the solids studied are either completely insoluble in the media or else (if a thin coating of molten metal acts as the medium) their solubility is low and, owing to the small mass of the coating, cannot lead to any substantial change in the specimen as a whole. Further, these effects relate to the surface of the metal itself, and are not due to the presence of oxide films, which can have only an incidental effect[5,20].

† In this review terms like deformation, strain, extension, etc. are often used synonymously (Ed. of Translation).

The development of a change in mechanical properties due to adsorption depends on several physicochemical factors, and primarily on the surface activity of the medium (or component) in relation to the given solid[6,11-14], i.e. on the absolute decrease in free surface energy resulting from adsorption. In addition, the experimental conditions — especially the temperature and the rate of deformation — profoundly influence the development on the effect[10,21-24]. Depending on these factors, the effect of surface-active substances on deformation and strength properties may take several quite different forms[13,14,24]. Thus an adsorption-active medium may soften the solid (metallic specimen); in such a case the yield point, and also the strain hardening in experiments with a constant rate of extension, is reduced or the rate of creep is increased in constant-load tests[5,23,24]. In other cases adsorption leads to the appearance of extreme brittleness in very plastic materials (single crystals of metals), accompanied by a sharp reduction in strength[11,12,22,25]. Under the influence of a strongly surface-active medium a solid may in certain circumstances show a tendency to disperse spontaneously into particles of colloidal dimensions[6,11-14].

Effects of the type under discussion find important practical application in the working of metals by pressure[26,27] and by cutting[28], in the find grinding of solids[7,8], etc. The study of these phenomena forms part of a new border-line science — the physicochemical mechanics of solids — developed by P. A. Rebinder and his collaborators, bordering on molecular physics, solid-state physics, physical chemistry, and the mechanics of continuous media. It has the aim of producing solids of specified structure and mechanical properties and of developing systematic methods for the mechanical working of solids by utilising physicochemical factors[6,29].

Single crystals of metals (including high-purity metals) provide the most interesting and also the simplest material for studying the effect of surface-active agents. In this case it proves possible to elucidate the most general and characteristic laws governing the observed phenomena, without complications due to grain boundaries, the presence of interfaces between different solid phases, and other subsidiary factors. At its present stage of development, the modern theory of the plastic deformation of crystalline solids — the theory of dislocations — which enables the mechanism of the action of the medium on the deformation and strength charaeteristics of a solid to be analysed[13-15,19,30], mainly in semi-quantitative terms, can be most usefully applied to materials of this kind. Such experiments will be examined in this survey.

2

The softening of metallic single crystals by organic adsorption-active media has been described in several papers[3-5,9]. Most authors have used dilute solutions of saturated and unsaturated aliphatic alcohols and acids and their substituted derivatives (i.e. substances whose molecules contain a polar group and a long hydrocarbon chain, such as oleic acid, palmitic acid, cetyl alcohol, etc.) in a non-polar hydrocarbon solvent (e.g. liquid paraffin). Experiments have been made on single crystals of tin, aluminium, and lead with extension both at a constant rate on a Polanyi type of apparatus and also under constant load. In the former case the effect of the medium is shown by a considerable decrease, almost to half, of the yield point (or crystal shearing stress) and of the strain-hardening (Fig. 1),

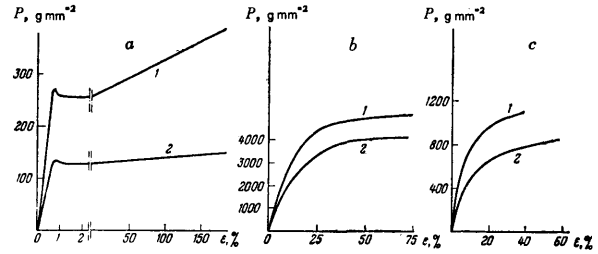


Fig. 1. Curves for the straining of single crystals: *a*) tin in an inactive medium (curve 1) and in a 0.2% solution of oleic acid (curve 2)[5]; *b*) aluminium in an inactive medium (curve 1) and in a 0.3% solution of cetyl alcohol (curve 2)[5]; *c*) lead in an inactive medium (curve 1) and in a 0.2% solution of palmitic acid (curve 2)[10].

TABLE 1. Values of the maximum softening effect and corresponding concentration of surface-active component for various organic surface-active media.

Medium	$\delta\epsilon_m$, %	c_m, moles kg^{-1}	Medium	$\delta\epsilon_m$, %	c_m, moles kg^{-1}
Octane as solvent			Dodecyl chloride	33	2.30
Propionic acid	123	0.59	Propyl sulphide	48	2.22
Octanoic acid	122	0.12	Aerosol OT	95	0.044
Stearic acid	126	0.0071	*Benzene as solvent*		
Oleic acid	190	0.0065	Propionic acid	120	3.90
Propyl alcohol	120	1.68	*Water as solvent*		
Dodecyl alcohol	118	0.20			
Octylamine	102	0.42	Propyl alcohol	49	4.10
Methyl laurate	38	1.50	Aerosol OT	no maximum	
			Aerosol MA		
			Sulfonol		

and in the latter case by a several-fold increase in the rate of plastic flow. Adsorption also changes the character of the slip lines on the crystal surfaces; this was particularly marked with single crystals of tin, which showed the characteristic phenomenon of a pronounced breaking up of the slip blocks on straining in an active medium[5].

The manner in which the magnitude of the softening effect depends on the nature of the polar group and the concentration of surface-active agent in the solution has been studied in detail in several investigations[5,31]. General rules were obtained governing the effect of surface-active substances on the deformation of metals as a function of the molecular properties and chemical structure of the former.

The external media used were the solvents octane, benzene and water, and solutions in them (concentration range 0–100%) of surface-active substances — aliphatic acids, alcohols, amines, ethers, halogenated and thio derivatives, soaplike colloidal electrolytes (sodium cetylbenzenesulphonate and dialkyl sulphosuccinate) and the wetting agents Sulfonol $C_{16}H_{33}.C_6H_4.SO_3Na$, Aerosol OT $C_8H_{17}OOC.CH_2.CH(SO_3Na).COOC_8H_{17}$, and Aerosol MA $C_6H_{13}OCC.CH_2.CH(SO_3Na).COOC_6H_{13}$. The hydrocarbons were carefully purified from polar impurities, and the surface-active substances were purified by repeated redistillation or recrystallisation.

The investigations were carried out on single crystals of tin and lead. The effect of the active medium was assessed from the relative increase in the deformation ϵ of the specimen in the surface-active medium compared with its deformation ϵ_0 in an inactive medium (the pure solvent) after the same periods of time, i.e. from the magnitude of $\delta\epsilon = [(\epsilon - \epsilon_0)/\epsilon_0] \times 100\% = f(c)$ during the creep of the single crystals, for solutions of different concentrations.

Solutions of surface-active substances in hydrocarbons (octane and benzene) exhibit in all cases a more or less sharply marked concentration optimum. As the concentration is increased, the effect rapidly reaches a maximum, and then gradually falls down to the lowest values in the pure surface-active component at $c = 100\%$.

Table 1 shows that the maximum effect $\delta\epsilon_m$ on single crystals of tin and the concentration c_m of surface-active component corresponding to this maximum are characteristically linked with the molecular properties of the active component. The magnitude of the effect in hydrocarbon media is determined solely by the nature of the polar groups in the surface-active molecules. The adsorption effect is most marked in solutions of aliphatic acids and alcohols in octane, its maximum value being almost the same, 120–125%, in the two homologous series.

A considerable adsorption effect is exhibited also by Aerosol OT and octylamine, $\delta\epsilon_m = 95\%$ and 102% respectively; a far smaller effect is exerted by compounds having weakly polar groups — esters and halogenated and thio derivatives — for which the values of $\delta\epsilon_m$ are 38% with methyl laurate, 33% with dodecyl chloride, and 48% with propyl sulphide respectively.

Further, the maximum effect at the optimum concentration is completely independent of the length of the hydrocarbon chain of the surface-active molecules. Independently of the position of the homologue in the series of aliphatic acids, the value of $\delta\epsilon_m$ remains unchanged at 122–125%, as is also found in the aliphatic alcohols. This result is consistent with the fact that hydrocarbon solvents, and in particular octane, are inactive with respect to tin.

Although the length of the hydrocarbon chains has absolutely no influence on the maximum value of the adsorption effect, the concentrations c_m, at which the maximum effect occurs, obey laws similar to Traube's rule, but with a smaller coefficient. As can be seen from Table 1, in the series propionic, octanoic, stearic acids, these concentrations are 0.59, 0.12, and 0.0071 mole kg^{-1} respectively, decreasing by a factor of 1.3–1.4 for each CH_2 group.

The decisive role of the polar groups in the surface-active molecules is also supported by the increased effectiveness of an unsaturated compound, oleic acid. Compared with stearic acid, the value of $\delta\epsilon_m$ has increased from 126% to 190%. Similarly, introduction of a double bond into the chain of an alcohol molecule markedly increases its activity (from 120% for propyl alcohol to 182% for allyl alcohol).

The efficiency of the surface-active substances is substantially affected by the molecular properties of the solvent. Replacement of octane by benzene shifts the concentration c_m at which the additive (propionic acid) gives its maximum effect from 0.59 to 3.9 moles kg^{-1}, i.e. increases it by a factor of 6.5, while the magnitude of the effect remains unchanged. In aqueous solutions, e.g. of propyl alcohol, interaction of the polar groups results not only in a shift of c_m (from 1.68 to 4.10 moles kg^{-1}) but also

in a decrease in the magnitude of the effect (from 120% to 49%). In this case the effect includes that of the solvent, water, which is an active medium with respect to tin and itself produces an effect amounting to 16%.

Similar regularities are observed with lead.

The above experimental data, which establish that the softening of metals depends on the composition of the external medium, not only confirm the purely adsorptive nature of the effect but also show that the influence of surface-active substances is characterised by laws typical of adsorption at liquid interfaces. In adsorption from solutions in hydrocarbons at a boundary with water, the surface activity of organic molecules is determined mainly by the work required to expel their polar groups from the solution at the interface, and the length of the hydrocarbon chains, solvated by the hydrocarbon medium, has a very slight effect[32]. These measurements were carried out with water-insoluble higher homologues of surface-active substances, thereby avoiding their distribution between the phases and the possibility of any appreciable adsorption from the aqueous phase. The deformation behaviour of tin and lead in organic surface-active media is likewise characterised by complete insensitivity to hydrocarbon molecules. This provides the grounds for drawing an analogy between adsorption from hydrocarbon solutions at the boundary with water and at metal surfaces.

Comparison of the isotherms for the reduction in surface tension, $\Delta\sigma = f(c)$, at the interface between water and solutions in octane with $\delta\epsilon = f(c)$ isotherms for the active substances investigated on tin and lead indicate the complete similarity of the laws governing the effects of adsorption-active substances on the free energy of liquid interfaces and in facilitating the deformation of metallic single crystals.

These laws are as follows:

(*a*) The polar groups of surface-active molecules are arranged in the following sequence of effectiveness:

$$COOH \simeq OH > NH_2 \gg S \simeq COOR > Cl.$$

(*b*) The deformation activity in homologous series increases according to Traube's rule with the same low coefficient 1.2–1.3 as with the surface activity in octane, in which it is 1.1–1.2.[32]

(*c*) Double bonds in the hydrocarbon chains of surface-active molecules behave as weak polar groups, and therefore strongly increase the surface activity of the compound.

(*d*) In benzene, which is more strongly polarisable than octane, the surface activity of organic compounds is markedly depressed[33], and in conformity with this the deformation activity of solutions of surface-active substances is lower in benzene than in octane. In a polar solvent, water, the deformation activity of surface-active substances falls markedly. This reduction in the energy of interaction of adsorbed molecules with a metal surface is quite consistent with the fact that the polarisation of polar groups in water and their hydration[34] considerably depress the surface activity of organic substances in aqueous solutions.

These results show that attempts[35-37] to explain the influence of an external surface-active medium on the deformation of metals in purely chemical terms are quite unjustified. But the data cited are still insufficient to explain completely the occurrence of maxima in the isotherms for the softening of metals. Several papers[5,10,23,24] have also been concerned with the variation of the softening action of the medium with temperature and rate of deformation.

In analysing the mechanism of the softening action of organic surface-active media, the following facts must be taken into account[14]:

1. Since normal diffusion of large organic molecules within a metal is impossible, and since they can penetrate into a metal only along structural defects (walls of micro-cracks) by two-dimensional migration, the effect must be based on purely surface interaction between the specimen and the medium. This interaction is shown by a diminution in the free energy σ of the surface of the specimen, brought about by reversible adsorption from the surrounding medium.
2. Compared with the free surface energies of the metallic single crystals used ($\sim 500-1000$ ergs cm^{-2}), the decreases produced in these experiments by adsorption of organic substances are not very great; they are of the order of several tens of ergs cm^{-2}, i.e. they do not exceed 10% of the original value of σ.
3. The softening action is usually observed within definite limited ranges of temperature and rate of deformation[10], and is therefore due to some thermally activated process. At each temperature there is a corresponding optimum rate of deformation, producing a maximum effect (Fig. 2).

Since plastic flow of a crystal is a process of displacement of dislocations along slip planes and their emergence at the surface, while the softening effect is produced by purely surface phenomena, the fundamental cause of the observed effect must obviously be regarded as the interaction between the dislocations and the free surface of the crystal[13,14,16,19].

A dislocation, being a thermodynamically unstable defect (possessing an excess of free energy), tends to emerge at the surface of a crystal. Application of the theory of elasticity enables an estimate to be made of the force with which an edge dislocation situated parallel to the surface is attracted to the surface: this force (the so-called "mirror-image

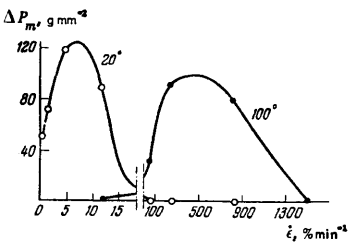


Fig. 2. Dependence of the magnitude of the adsorption effect on the rate of strain ϵ for single crystals of tin at different temperatures[10]. The magnitude of the effect ΔP_m is expressed as the difference between yield points in inactive and in active media.

force") is inversely proportional to the distance from the surface; i.e. it is determined by a slowly varying logarithmic potential[38]. Further, emergence of the dislocation (i.e. completion of its displacement in a given slip plane) is accompanied by the appearance of steps, the width of which at a given point on the edge of the slip plane is equal to the component of the Burgers vector lying in the slip plane normal to the edge. The creation of each new surface step requires work to be done $\leq b^2\sigma$, where b is the Burgers vector (unit translation). This potential barrier extends inside the crystal only to a distance of about half the width of the dislocation (of the order of a few b); i.e. it is quite steep, and in the immediate vicinity of the surface the force due to it, opposing emergence of the dislocation, may prevail over the expulsive "mirror-image force"[19].

Let us consider a point M on the edge of an active slip plane, at which the Burgers vector is perpendicular to the edge and the step reaches its maximum width of $\sim b$. During plastic flow of the crystal, v dislocations pass through this point per second, and passage of each of them creates in the region of M a new surface of $\sim b^2$, possessing a free energy of $\sim b^2\sigma$. In the absence of applied stresses, this quantity must apparently be regarded as the activation energy of the process.

The condition that the numbers of dislocations approaching and leaving the point M should be equal is then expressed by the equation

$$v = \nu \exp(-U/kT),$$

where $\nu \simeq 10^{12}-10^{13}$ sec^{-1} is the Debye lattice vibration frequency and the quantity U is equal to $b^2\sigma$ less the work A done by external forces. The temperature defined by this relationship, $T_1 = b^2\sigma/k \ln(\nu/v)$, then represents the "upper temperature limit" for the existence of this potential barrier: at $T \gg T_1$ emergence of dislocations at the crystal surface does not require the application of any considerable additional forces; at lower temperatures work must be done by external forces. Thus in the neighbourhood of T_1, when A is small, it can be expected that even a slight decrease in σ, reducing A to zero, will have the greatest effect on the plastic properties of the crystal; i.e. that the optimum temperature for the softening effect is $T_{opt} \simeq T_1$.

The parameter v introduced into the discussion is determined by the rate of deformation and its microheterogeneity (localisation of displacements in a series of slip lines), and for average orientations of the crystals can be approximately evaluated as follows[15,18,29]: $v \simeq \dot{\epsilon}hu/b$, where $\dot{\epsilon}$ is the rate of strain, h is the mean distance between the slip lines, and the deformation microheterogeneity factor u represents the ratio of the total number of slip lines to the number which are active at any particular instant (in general, the values of hu can vary within quite wide limits, e.g. from 10^{-1} to 10^{-3} cm).

With the above model, the optimum temperature for the softening effect thus proves to be related to the rate of deformation in the following fashion[14]:

$$T_{opt} \simeq \frac{b^2\sigma}{k \ln(\nu b/\epsilon hu)}. \quad (1)$$

When $\dot{\epsilon} = 10\%$ min^{-1}, the logarithmic term in the denominator is $\sim 20-25$, and substitution of $b = 3 \times 10^{-8}$ cm and $\sigma = 10^3$ ergs cm^{-2} gives a value of $\sim 0.5-0.6$ eV for the activation energy, which means that under these conditions $T_{opt} \simeq 300°$K; increasing $\dot{\epsilon}$ by a factor of 100 should raise T_{opt} to about 400°K.

This result is in good agreement with experimental data[10] for the reduction of the yield point of single crystals of tin (see Fig. 2), according to which the adsorption effect is a maximum at room temperature if the rate of straining $\dot{\epsilon} = 5-10\%$ min^{-1}, and at 100° if $\dot{\epsilon} \simeq 500\%$ min^{-1}.

Subsurface sources of dislocations (anchored at a single point) may play a significant part in producing the softening effect, as the force required to set them in operation is considerably less than with sources having two pinning points[39]. A thin polycrystalline film deposited on the surface of a single crystal, and also the alloying of a thin surface layer, can appreciably raise the yield point of a specimen, by impeding the operation of these sources[40-42]. On the other hand, a decrease in σ can naturally be expected to increase the activity of the subsurface sources and to lower the yield point. Since interaction of such a source with the surface is in effect a successive "drawing" of the second (unanchored) end of the section of the dislocation along the crystal surface, i.e. the formation of a step on the surface, relationship (1) remains valid; the parameter v retains the same order of magnitude, but acquires the sense of the number of turns per second of the subsurface source (the dislocation spiral in the Frank–Read mechanism[38]).

The above model cannot be directly applied, however, to the softening of metallic single crystals by molten metal coatings at elevated temperatures and very low rates of strain[23,24] (see below): in such a case the parameters entering into relationship (1) (activation energy, vibration frequency) evidently have a rather different physical meaning and magnitude. It is quite possible that interaction of dislocations with surface defects blocking individual points on the edge of the slip plane here plays an important role; the potential barrier then becomes higher and acquires a different expression, but remains as before short-range in effect and substantially dependent on σ.

The mechanism of the action of an adsorption-active medium may also be connected with a process of generation of dislocation sources. However, the question of the generation of sources is still not absolutely clear, and the influence of the magnitude of σ on this process is even less clear.

Thus the softening effect, which represents only one of the cases of the action of adsorptive-active media on the mechanical properties of a solid, is itself complicated and varied, being connected with the existence of a whole spectrum of activation energies, and can be observed over different ranges of temperature and rate of deformation.

3

Organic media are feebly surface-active: as was noted above, the decrease in free surface energy accompanying adsorption from such media is only several tens of ergs cm^{-2}. Rebinder and his collaborators have shown that melts of other, more readily fusible metals (and probably also of some salts and other compounds) are incomparably more active with respect to metals[6,11,12,22,25]. In this connection the work of Kishkin and Potak[43-46], in which the adsorption character of the reduction in strength of metals by readily fusible metallic melts is stressed, is of great interest.

The laws governing the action of such strongly surface-active media on the deformation and strength properties of single crystals of various metals have been studied in a series of investigations carried out during recent years in the Disperse Systems Section of the Institute of Physical

Chemistry of the Academy of Sciences of the USSR and in the Department of Colloid Chemistry of the Moscow State University. This work has shown that in the presence of strongly adsorption-active media a qualitative change in the mechanical properties of the metal may occur: a highly plastic metallic single crystal, capable of being deformed by several hundred per cent, will become brittle, its strength falling sharply. This type of effect is exerted by molten tin on single crystals of zinc and cadmium[11,12], by mercury on single crystals of zinc[22,47-50] and tin[21,22,24,51], and by liquid gallium on zinc[17,25], cadmium[25], and tin[52].

The single metal crystals which formed the subject of the investigations were grown by zone crystallisation[53] from extremely pure preparations (containing 99.99% and 99.999% of the main metal), and in a few cases, in order to study the effect of impurities, from technical materials, or from the pure metal containing a small admixture of another metal[49,50]. The specimens had a diameter of 0.5–1.0 mm and a wide range of crystallographic orientations. The adsorption-active metal was deposited on the surface of the specimens in the form of a thin coating (usually a few microns thick) either electrolytically[11,12], chemically (by displacement from a salt solution[22,47-50]), or mechanically[25,52].

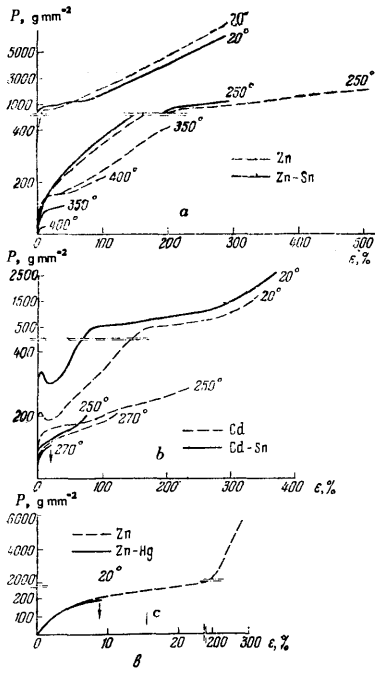


Fig. 3. Variation of true tensile stress P with strain ϵ: *a*) for single crystals of zinc with and without a tin coating; initial orientation of crystals $\chi_0 = 44°$ and rate of strain $\dot{\epsilon} = 15\%$ min^{-1};[12] *b*) for single crystals of cadmium with and without a tin coating; initial orientation of crystals $\chi_0 = 39°$ and rate of strain $\dot{\epsilon} = 15\%$ min^{-1};[12] *c*) for single crystals of zinc with and without a coating of mercury; initial orientation of crystals $\chi_0 = 48°$, rate of strain $\dot{\epsilon} \sim 15\%$ min^{-1}.[15]

Coated and uncoated specimens were strained over a wide range of temperatures and rates of deformation both on a Polanyi type of apparatus and under constant load. The main results obtained in these experiments are indicated below.

At temperatures above the melting point of the metal–coating eutectic, the presence of a thin molten layer of surface-active metal leads to a great reduction in the plasticity and strength of the specimen (Fig. 3); the character of the fracture also changes: from being plastic in air it becomes brittle in the presence of a surface-active coating. Thus single crystals of zinc at room temperature can usually be deformed by several hundred per cent, stretched into a thin strip, and broken with the formation of a neck at stresses of ~ 5 kg mm^{-2}; after amalgamation, the limiting deformation is reduced to 10% (or below) and fracture occurs at stresses of ~ 200 g mm^{-2} (and below), with a mirror-like cleavage on the (0001) plane[22,47-50]. Molten tin has a similar effect on the limiting deformation and the breaking stress of single crystals of zinc and cadmium; mercury acts in the same way on single crystals of tin at sufficiently high rates of deformation[21,22,24,51].

With respect to zinc, liquid gallium is evidently a still more strongly surface-active medium than tin and mercury: the limiting deformation in this case reaches only a few per cent or even fractions of one per cent[25]. A specially interesting case is provided by the cadmium–gallium system[25]: single crystals of cadmium are extremely plastic even at very low temperatures and high rates of deformation, and give no cleavage on the slip plane; on application of gallium, however, the same single crystals undergo brittle fracture at room temperature and relatively low rates of extension ($\sim 200\%$ min^{-1}), with mirror-like cleavage on the basal plane.

The development of the embrittling action of a surface-active metallic melt depends greatly on the temperature and the rate of deformation[11,12,15,19,21,22,51]. When the temperature falls below the melting point of the metal–coating eutectic, the effect gradually disappears, obviously because the mobility of the adsorption-active atoms is reduced and their rapid migration along freshly developing surfaces becomes impossible. This is the lower temperature limit of the embrittling effect.

There exists also an upper temperature limit, whose position for a given metal–coating pair depends to a considerably greater extent on the rate of deformation. Thus in the case of amalgamated zinc at ordinary rates of strain ($\sim 10\%$ min^{-1}) the plasticity and the normal strength are reestablished when the temperature is raised to $T_c \simeq 150°$ (Fig. 4); within a relatively narrow range of transition temperatures, $\Delta T \simeq 40°–50°$, a peculiar "partial embrittlement" is observed, in which the specimen, covered with deep, half-opened cracks, nevertheless shows considerable deformability. When the rate of deformation is decreased, the transition region between brittleness and plasticity is shifted to lower temperatures. The presence of alloying impurities in the single crystal acts in the opposite direction and raises the transition temperature T_c.

In the case of zinc–tin, the embrittling effect at strain rates of $\sim 10\%$ min^{-1} extends from the melting point of the coating right up to the melting point of zinc[11,12] (in other words, the transition temperature T_c would seem to be above the latter); furthermore, the effectiveness of the coating actually increases in this case when the temperature is raised (see below). When the rate of deformation is reduced to $\sim 10^{-4}$ min^{-1}, however, the brittleness dis-

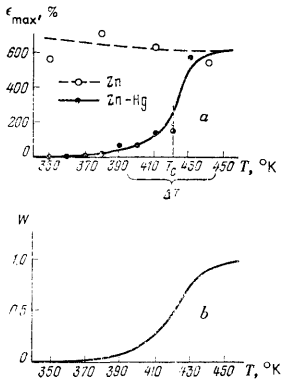


Fig. 4. *a*) Dependence of the limiting strain at fracture ϵ_{max} on temperature for single crystals of zinc with and without a mercury coating at $\chi_0 \sim 45°$ and $\dot{\epsilon} = 15\%\ min^{-1}$; *b*) theoretical curve for the temperature variation of the "probability of plastic flow" for amalgamated single crystals [15,22].

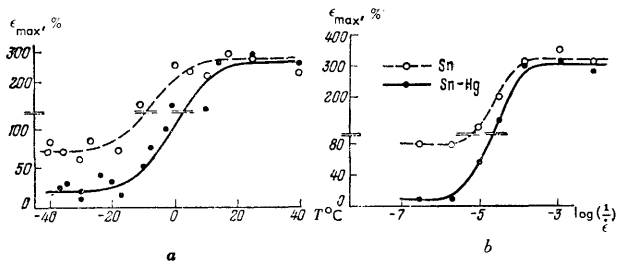


Fig. 5. *a*) Temperature dependence of the limiting strain at fracture ϵ_{max} for single crystals of tin with and without a mercury coating when $\dot{\epsilon}$ = const.; *b*) dependence of ϵ_{max} on rate of strain $\dot{\epsilon}$ when T = const. [21,51]

appears at all temperatures [22] (i.e. the transition temperature T_c falls below the melting point of the coating, but the coating is then already solid, and the effect is absent).

In the case of tin–mercury, the embrittling action of the coating on single crystals grown from extremely pure metal is distinct and reproducible at room temperature only at very high rates of strain (up to 10^5–$10^6\%\ min^{-1}$); but if the rate of deformation is low, the transition temperature T_c is around 0° or lower (see Fig. 5). Evidently this peculiar position of T_c is responsible for the fact that the development of the embrittling action of mercury on single crystals of tin at room temperature is very sensitive to the purity of the tin.

The following facts play a large part in elucidating the mechanism of the embrittling action of a molten coating:

1. The decrease in free surface energy at the interface between a metal and its saturated solution in another, liquid metal may be very considerable [6,11,12,14] — hundreds of ergs per cm^2.
2. Since we are concerned with the development of fractures within the crystal, this is a bulk effect and requires rapid penetration of adsorption-active atoms to the surface of the internal micro-voids by anomalous diffusion (migration) along structural defects in the crystal [14,15].
3. The effect appears practically immediately after application of the coating to the single crystal; consequently, normal (bulk) diffusion is not the decisive factor here.
4. With an appropriate rate of deformation, the effect is observed over a wide range of temperatures from the melting point T_m of the coating (more exactly, of the metal–coating eutectic) up to the melting point T_M of the main metal or the transition temperature T_c, and the magnitude of the effect is independent of temperature within this range. This suggests that the process of brittle fracture due to the presence of the coating is not by itself thermally activated†.
5. The transition from brittleness to plasticity in the presence of a coating is very similar (especially in the case of zinc–mercury) to the analogous transition in the absence of a coating occurring at lower temperatures; this latter transition may be termed the "threshold of natural cold-shortness", in contrast to the threshold displaced to higher temperatures, that of "imposed cold-shortness", due to the action of the adsorption-active medium. It may be assumed that, other things being equal, the position of this threshold is determined primarily by a single parameter — the magnitude of the free surface energy σ. [21]

Thus an elucidation of the mechanism of the embrittling action of a strongly adsorption-active medium on metallic crystals must start from an analysis of the mechanism of the brittle fracture of these crystals in the absence of such a medium; a description of the conditions for the transition from brittleness to plasticity in the presence of a coating must likewise be correlated with the analogous phenomenon for the pure metal.

At the present time the most detailed data are available for zinc–mercury [22,42,47-50], and they will be mainly used in discussing the mechanism of the embrittling action of the medium.

It has been shown convincingly in several papers that, even at very low temperatures, brittle fracture of single crystals of zinc along a cleavage plane is not perfectly brittle, in the sense that it is always preceded by some plastic deformation [47-50,54,55]. At the temperature of liquid nitrogen and normal rates of deformation of $\sim 10\%\ min^{-1}$, the limiting

† The increase in the effect with temperature in the case of zinc–tin (at ordinary rates of extension and relatively high temperatures) is evidently associated with a sharp increase in the solubility of zinc in tin, and hence with a further fall in the free surface energy at the metal–melt boundary; indeed, when the concentration of the main metal in the liquid metallic coating becomes high, conditions at the phase boundary approach those at the metal–melt boundary in a single-component system, and in this case the free interfacial energy may be only several tens of ergs cm^{-2}.

displacement a_c in the a_0 direction for specimens of diameter $L_0 \simeq 1$ mm is within the range from several to several tens per cent, depending on the initial orientation of the crystal [the angle χ_0 between the axis of the specimen and the slip plane (0001), which in this case coincides with the cleavage plane]. The relation between a_c and χ_0 for the fracture of single crystals of zinc at liquid-nitrogen temperature is exactly opposite in character to that observed at ordinary temperatures (without any coating): in the former case a_c falls abruptly with rise in χ_0, whereas in the latter case a greater crystallographic displacement a_c corresponds to greater angles χ_0 (Fig. 6).

Zonke's law, which states that single crystals with different orientations undergo brittle fracture when the stresses normal to the cleavage plane reach a definite value p_c = = const., proves to be completely inapplicable to the fracture of single crystals of zinc at the temperature of liquid nitrogen. With increase in the angle χ_0, in fact, the values of p_c increase sharply (Fig. 7*a*), while the values of the shearing stresses τ_c reached at the instant of fracture decrease substantially (approximately in inverse proportion to the increase in p_c). Exactly similar regularities are observed for the fracture of amalgamated single crystals of zinc at room temperature (Fig. 7*b*), but the values of p_c and τ_c are then less than half. The fracture of single crystals of zinc and cadmium in the presence of liquid gallium follows analogous rules[22].

The actual breaking stresses p_c in the cleavage planes are smaller by several powers of ten than the so-called "theoretical" value, $p_{theor} \simeq (E\sigma/b)^{\frac{1}{2}}$, calculated on the basis of some model of the interatomic forces for an ideal crystal lattice containing no imperfections; here E is Young's modulus, σ the specific free surface energy, and b a lattice constant. This discrepancy is usually related to the presence in a real crystal of various structural defects, primarily micro-cracks. The fact that Zonke's law is not obeyed, and the observed dependence of a_c, p_c, and τ_c on χ_0 for the brittle fracture of single crystals of zinc, enable us to make the following step towards explaining the mechanism of brittle fracture and specifying the role of p and τ more exactly[30].

It is reasonable to assume that, in plastic flow under the action of shearing stresses τ, defects arise and develop, and then, on reaching certain dimensions and with an appropriate value of the normal (tensile) stress p_c, become "dangerous", i.e. lead to the appearance of macroscopic cracks, which spread throughout the cross-section of the crystal. In such a case at least two main stages are to be distinguished in the process of fracture:

Stage *A*: Plastic deformation preceding the appearance of dangerous cracks (which in turn can evidently be divided into several different substages).

Stage *B*: A more or less rapid spreading throughout the specimen of one or several dangerous cracks which are close together and merge into one another.

In the case of brittle fracture, the start of stage *B* is very clearly marked, and itself occurs with extreme rapidity.

In stage *A* the shearing stresses and the resulting plastic deformation play the principal role. It is highly significant here that the plastic deformation of a crystal always develops with great inhomogeneity, both in space (in the body of the crystal) and in time. Spatial inhomogeneities consist in the localisation of deformation in

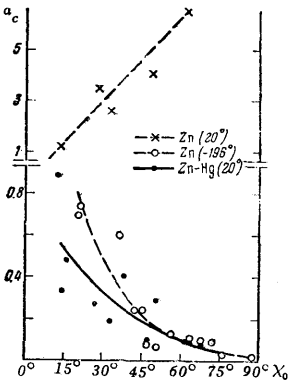


Fig. 6. Dependence of the limiting displacement of a_c on orientation for single crystals of zinc with and without a mercury coating, χ_0 being the initial value of the angle between the basal plane and the axis of the specimen[47–50].

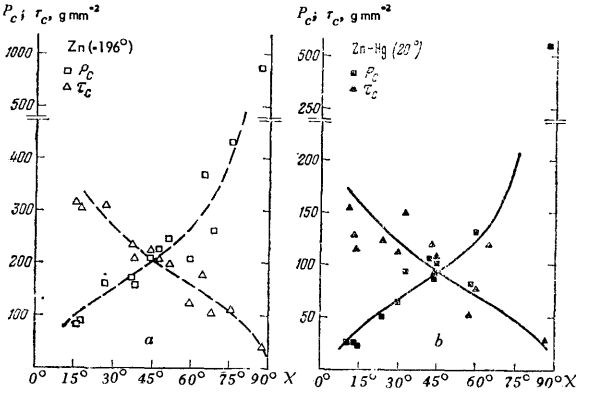


Fig. 7. Orientation dependence of normal (p_c) and shearing (τ_c) stresses at fracture for single crystals of zinc: *a*) without coating at temperature of liquid nitrogen; *b*) with a mercury coating at room temperature. The angle χ is that between the basal plane and the axis of the specimen at the instant of fracture. Purity of the material 99.999% and 99.99% Zn.[15,30,49,50]

narrow slip lines (or bands), the propagation of these lines to only part of the edge of the slip plane (i.e. the accumulation of incomplete, local displacements in the crystal), fragmentation and block formation in the crystal, the appearance of deformation and kink bands (fault formation), the occurrence of twin boundaries, etc. The temporal inhomogeneity of deformation is shown, for example, by slip lines appearing at different times, and by various advances and delays in the process, right up to clearly defined sudden changes in deformation, etc.

Micro-heterogeneities in deformation are closely connected with the dislocation nature of plastic flow. Local deformations may reach very high relative values and lead to considerable local disturbance of the crystal lattice, a marked weakening of the bonds in the lattice over a more or less appreciable distance (i.e. to the appearance of centres of disintegration with some effective dimensions c), and also to the formation of new barriers opposing slip — sub-boundaries (dislocation networks), pinned dislocations, stacking faults, twin boundaries, etc. Furthermore, certain kinds of micro-heterogeneities in the deformation, including incomplete slip which has not spread over the whole cross-section of the crystal (i.e. dislocations piled-up in a single slip plane, or in several closely adjacent planes against various obstacles), lead to the appearance of marked local stress concentrations, many times greater than the applied shearing stress τ [15,19,30,56,57]. These high local stresses may in turn lead to the formation and gradual extension of micro-cracks, which are equilibrium centres of breakdown (the term "equilibrium" is understood to mean here that the magnitude c of a given defect, with the existing level of applied normal stress, has not yet reached at stage A the critical value at which the defect becomes dangerous and spreads over the whole crystal in the form of a fracture)†.

The character of the centres of disintegration and the extent of their development (the effective quantity c) at different substages of stage A depend essentially on the nature of the crystal and the conditions under which deformation occurs. In the case of pure basal slip in single crystals of zinc at low temperatures, as well as at ordinary temperatures, the following scheme can be used for the initial substages of deformation — i.e. for not very high values of displacement a and shear stress τ — when the process of relaxation of local deformations and high stresses is not sufficiently effective††.

Let us suppose that a shear stress τ has caused a displacement Δ in a slip plane, and that this displacement has not extended over the whole cross-section of the crystal owing to the presence of some sufficiently strong ("insurmountable") obstacle O in the slip plane (Fig. 8)†††. The main region of localisation of the displacement is then the distance $MO = s$ along the slip plane.

The magnitude of s obviously depends on the initial slip Δ, which in turn is determined by the overall plastic strain a reached by that instant. From the point of view of elucidating the cause of fracture of the crystal, we are primarily interested in the greatest possible value, $s_{max} = L$, under the given conditions. In a well annealed crystal $L = 0$. It may be assumed that, during the first substage of stage A, the quantities Δ and L increase monotonically with increase in the displacement a, at first very rapidly, then more slowly. This substage (A') is characterised by a high value of the strain-hardening factor and the accumulation in the crystal of the relatively large elastic energy of the heterogeneities which are formed. At some value of the crystallographic displacement $a = a_0$, corresponding to the shear stress τ_0 on the deformation curve, limited slip ceases, since the elastic strain field thereby set up, which opposes displacement along the given slip plane, becomes so intense that, at the given level of shear stress, further slip can proceed more readily in other sections of the crystal, which do not contain such strong obstacles. It is evident that L may then reach values of the same order of magnitude as the diameter L_0 of the single crystal.

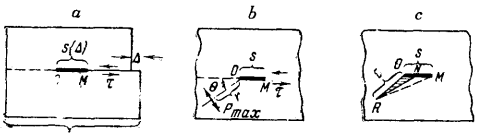


Fig. 8. *a*) Appearance of limited slips; *b*) concentration of normal stress near region of limited slip; *c*) appearance of a micro-crack in the region of maximum concentration of tensile stress [30].

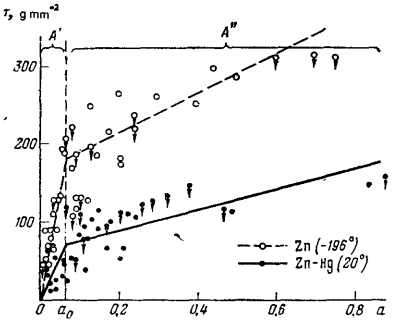


Fig. 9. Dependence of shear stress τ on the crystallographic displacement a for differently oriented single crystals of zinc without any coating (at the temperature of liquid nitrogen) and with a mercury coating (at room temperature). The arrows indicate the points corresponding to the instant of fracture; the broken lines correspond to the averaged form of the τ (a) curves. Purity of material 99.999% and 99.99% Zn. [49,50]

The displacement a_0 at which substage A' finishes corresponds to a characteristic break in the deformation curve for the single crystal (Fig. 9). The next substage A'', during which the maximum variation in the displacement changes considerably more slowly, is characterised by an appreciable decrease in the strain-hardening factor.

The stress field around the defect of extent $MO = s(\Delta)$ may be likened to the elastic field of a notch of length s parallel to the applied shear stress τ. The theory of

† An "equilibrium" crack in this sense of the word is not, of course, reversible; when the tension is removed, the crack generally remains.

†† It is essential that this should occur even if in only a single slip band; it is just here that a centre of breakdown will then develop to a dangerous size.

††† In the present case, where we have several horizontal dislocations lying in a single slip plane, or in a few such planes close together, the obstacles may be pinned dislocation, vertical wall dislocations (tilt boundants with a small angle of disorientation), etc.

elasticity shows[57,66] that the maximum tensile stress then arises along a line inclined at an angle θ to the plane of the notch, reaching a value $p_{max} \sim \tau(s/r)^{\frac{1}{2}}$, r being the distance of the point from the apex of the notch.

Let a crack *NOR* of length c (see Fig. 8) be formed in the region of maximum stress concentration. These high stresses will then be relaxed over an area of $\sim cs$. In the absence of a crack, the density of elastic energy in the region of the gap *MO* would be $w = p^2/2E \simeq \tau^2 s/2Er = w(r)$. The decrease in energy entailed in opening the crack (per unit length in a direction perpendicular to the plane of the paper) is roughly $(\tau^2 s^2/2E) \ln(c/r_0)$; here the lower limit of integration r_0 (of the order of a few b) is determined by the inapplicability of the relationships of the theory of elasticity in the immediate vicinity of point O, and b is the repeat distance of the lattice.

At the same time, formation of the crack requires that work of $\sim 2c\sigma$ should be done to produce the new free surface. The net increase in energy is $\Delta W = 2c\sigma - (\tau^2 s^2/2E) \ln(c/r_0)$. The function $\Delta W(c)$ has a minimum at $\partial(\Delta W)/\partial c = 2\sigma - \tau^2 s^2/2Ec = 0$. Hence accumulation of limited slip over a distance of $s = s(\Delta)$ in the slip plane may produce an equilibrium V-shaped crack of magnitude $c \simeq \tau^2 s^2/4E\sigma$ in the crystal. Since we are interested in the maximum possible length c, the value $s_{max} = L(a) \leqslant L_0$ must be substituted in the resulting expression.

A completely analogous expression for c may be obtained in terms of the theory of dislocations, since the limited slip Δ is obviously the same as a set of $n = \Delta/b$ dislocations. Actually $n \simeq \pi(1 - \mu)L\tau/Gb$, where G is the shear modulus and μ is Poisson's ratio[58]; the coalescence of n dislocations produces a crack of length[57]

$$c \simeq n^2 Gb^2/8\pi(1 - \mu)\sigma, \text{ i.e. } c \simeq \{\pi(1 - \mu)/8\}(\tau^2 L^2/G\sigma).$$

It can thus be assumed that application of a shear stress τ in a slip plane in a crystal may produce an equilibrium crack up to $c = \beta\tau^2 L^2/E\sigma$ in size, where the dimensionless coefficient β does not differ greatly from unity, and L increases monotonically during the first substage of stage A from zero to some final value approaching the diameter L_0 of the crystal, which is greater, the greater the displacement a_0 in the given substage A'. †

The actual start of an incipient micro-crack having as yet no fully developed free surface may be imagined as a process of combination of the primary (leading) dislocations of the set to form a narrow, hollow dislocation nucleus[15,19,65]. Such hollow nuclei can evidently be formed at very low values of τ and a, and play a large part in the penetration of adsorption-active atoms inside the crystal. With increase in τ an equilibrium micro-crack of size $c = c(\tau)$ gradually develops. In the case of zinc the fissures in the basal plane then alternate with those in the prismatic plane; ultimately, the direction of extension of the crack is close to the basal plane[14,15,30].

We have thus considered stage A, preceding fracture, the main part in which is played by the shear stress and the inhomogeneity of plastic deformation.

In stage B, which is extremely short-lived in the case of brittle fracture, the normal stress has the decisive role. Stage B ensues when the displacement a_c is such that the stress p normal to the plane of the crack [in this case the (0001) plane] is sufficient to make the crack dangerous and non-equilibrium, i.e. when $p_c(c) = \alpha(E\sigma/c)^{\frac{1}{2}}$, where α is some dimensionless coefficient which differs little from unity[15,59].

On substituting the value found for the maximum possible size of crack $c(\tau)$ in the expression for $p_c(c)$, we obtain the following relationship[29] instead of Zonke's law:

$$p_c\tau_c = K^2; \quad K = \gamma'\sqrt{E\sigma/L} = \gamma\sqrt{G\sigma/L}, \qquad (2)$$

where the dimensionless coefficients γ' and γ are close to unity in magnitude, and K is constant at stage A'' and increases when $a_c < a_0$. The resulting relationship may be called the "condition of constant product of normal and shear stresses" during brittle fracture.

In combination with the "geometrical" conditions $\tau_c = P_c \sin\chi \cos\chi$, $p_c = P_c \sin^2\chi$, and $p_c/\tau_c = \tan\chi$, where P_c is the true tensile stress and χ is the angle between the basal plane and the axis of the specimen at the instant of fracture, we find that

$$p_c = K\sqrt{\tan\chi}; \quad \tau_c = K\sqrt{\cot\chi}; \quad P_c = K \sin^{-3/2}\chi \cos^{-1/2}\chi. \dagger \qquad (3)$$

The relations (3) are well satisfied both for the fracture of single crystals of pure zinc at the temperature of liquid nitrogen††, and for the elongation of amalgamated single crystals at room temperature (Fig. 10)[14,15,30,47-50]. The values of $K = (p_c\tau_c)^{1/2}_{av} \equiv (P_c \sin^{3/2}\chi \cos^{1/2}\chi)_{av}$ obtained from the experiments are 209 g mm^{-2} in the former case and 95 g mm^{-2} in the latter, which according to (2) correspond to a decrease in the free surface energy of zinc in the presence of mercury roughly by an amount

$$\sigma_{Zn-Hg} = \sigma_{Zn}/(K_{Zn}/K_{Zn-Hg})^2 \sim 10^3/(209-95)^2 \sim 200 \text{ ergs cm}^{-2}$$

The good agreement of experimental values of P_c for differently oriented single crystals with condition (3) shows

† An extremely rough estimate of a_0 may be obtained as follows. Since $\Delta/s \sim \tau/G$, the maximum value Δ_{max} for $s \sim L_0$ is $\sim L_0\tau/G \sim 10^{-5}$ cm (the accumulation of several hundred dislocations); on the other hand, at the end of substage A', the value of Δ_{max} is evidently not very much greater than that of $a_0 h$, where h is the distance between the slip lines. Assuming that $a_0 \sim \Delta_{max}/h$, we find that when $h \sim 10^{-3}$ cm, $a_0 \sim 10^{-2}$, which is roughly of the same order of magnitude as that given by the experimental data (see Fig. 9).

† In this scheme the dimensions of the slip plane are identical with the diameter of the single crystal, which is actually merely the minor axis of a slip plane in the shape of an ellipse; this means, in essence that relationships (2) and (3) relate to the propagation of strain inhomogeneities along the minor axis of an ellipse, i.e. to groups of screw dislocations. In the case of edge dislocations the maximum size of the region of localisation of the strain inhomogeneities must be taken as the major axis of the ellipse. Conditions (2) and (3) are then written in the form

$$p_c\tau_c = K^2 \sin\chi_0; \quad p_c = K \text{ tg}^{1/2}\chi \sin^{1/2}\chi_0 \text{ and } \tau_c = K \text{ ctg}^{1/2}\chi \sin^{1/2}\chi_0.$$

This fact may be linked with some observed deviations from the condition that $p_c\tau_c$ should be constant, especially at small angles χ, as well as with the considerable scatter of the experimental results. Comparison with experiment shows, however, that the condition $p_c\tau_c = \text{const.}$ is quite acceptable as a first approximation.

†† According to (2) $K \propto L^{-\frac{1}{2}}$; since at stage A'' the value of L approaches the order of magnitude of the diameter L_0 of the single crystal, and for a given degree of purity of the material is apparently a definite fraction of L_0, it may be assumed that $K \propto L_0^{-\frac{1}{2}}$. In fact, this is confirmed both in our own experiments[47,50] and by comparison with the data of other workers[54,55] on the brittle fracture of single crystals of zinc at low temperatures[49,50].

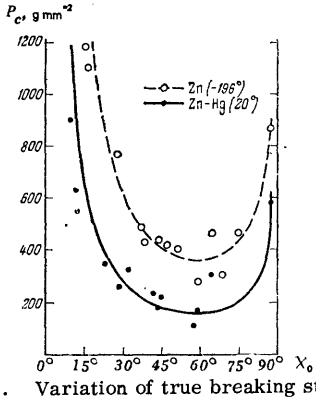


Fig. 10. Variation of true breaking stress P_c with orientation for single crystals of zinc without a coating (at the temperature of liquid nitrogen) and with a mercury coating (at room temperature); the curves correspond to the condition $P_c\tau_c$ = const. Purity of material 99.999% and 99.99% Zn.[49,50]

TABLE 2. Experimental values of the quantity K and of the strain a_0 corresponding to the yield point in the $\tau(a)$ curve for single crystals of zinc of differing purity without a coating (at the temperature of liquid nitrogen) and with a mercury coating (at room temperature)[49].

Purity of zinc	Diameter of specimens L_0, mm	$K=(P_c \sin^{1/2}\chi \cos^{1/2}\chi)_{av}$, g mm^{-2}: non-amalgamated, at -196°	K: amalgamated, at 20°	a_0, %	$\frac{a_0}{a'_0}$	$f=\frac{K^2L'_0}{K^2L_0}$ at -196°
Zn 99.999% / Zn 99.99%	0.9 = L'_0	209 = K'	$\frac{92}{91}$	6 to 7 = a'	1	1
Zn +0.2%Cd	0.54	316	153	3	~0.5	0.72
Zn technical	0.9	263	124	2 to 3	~0.4	0.63
Zn +0.5%Cd	0.54	361	230	2	~0.3	0.5

that in these experiments fracture has occurred with $a_c > a_0$, when the process of forming inhomogeneities is in the main already complete, and L is approximately constant. Actually, the stress–strain curves exhibit in nearly all cases a more or less well developed stage A''. But if fracture takes place at very small strains $a_c < a_0$, as occurred in experiments[55] with single crystals of zinc of diameter 6 mm at extreme orientations $\chi \leqslant 60°$, stage A'' is not reached; the stresses P_c then prove to be greater than would follow from condition (3), and the values of $(p_c\tau_c)^{1/2}$ increase monotonically with decrease in a_c.[49,50]

Study of the laws of the brittle breakdown of alloyed single crystals of zinc[49,50] has shown that in this case the condition $p_c\tau_c$ = const. remains valid over a wide range of orientations, for the fracture both of specimens without a coating at -196° and of amalgamated specimens at room temperature (in both cases fracture generally occurred at stage A''). The strength increases to about the same extent with increasing content of impurity in the two cases (see Table 2); furthermore, the value of the strain a_0 corresponding to the yield point in the deformation curve (i.e. the extent of stage A') falls.

With other conditions the same, alloyed crystals are deformed more uniformly than are pure crystals, and their strain-hardening factors are considerably higher. Hence growth of local strains takes place less intensively in alloyed crystals, and ceases at lower values of a_0, than in the case of pure crystals. Thus at the same diameter alloyed crystals are characterised by a lower value of L at stage A'', as is confirmed by the data in Table 2.

Even in the case of alloyed specimens, where there is a general increase in K, values of K for amalgamated crystals fractured at room temperature prove to be roughly half (or somewhat lower) the values for uncoated specimens strained at -196°.

Thus, the concept of a considerable reduction in the free energy of new surfaces developed in the process of fracture explains, in good agreement with the experimental data, the sharp decrease in the plasticity and the strength of amalgamated single crystals of zinc. The above scheme is obviously applicable to the analysis of other metal–coating pairs, such as zinc–tin, cadmium–gallium, etc.

From a comparison of the metal–coating pairs investigated with the binary melting-point diagrams, a semi-empirical rule has been established, indicating whether or not a given metal M_1 is strongly surface-active with respect to a more refractory metal M_2.[17] This is that a reduction in strength due to adsorption, corresponding to a considerable decrease in σ, is observed when M_1 has a small but finite range of solubility in metal M_2 in the solid state. On the other hand, no effect is generally observed if this range is very wide, or if it is altogether absent.

4

As was noted above, the presence of a molten, strongly adsorption-active coating shifts the threshold of cold-shortness to substantially higher temperatures. With unamalgamated single crystals of zinc and normal rates of straining, the transition from brittleness to plasticity is observed at about -50°.[60] At this temperature the relaxation of inhomogeneities in the deformation (dislocation pile-ups) and of high local stress concentrations is sufficiently effective to decrease the size c of the equilibrium disintegration nuclei at the same level of sheer stress τ; K begins to increase. Furthermore, as a result of the decrease in the strain-hardening factor, the quantity $(p\tau)^{1/2}$ now reaches its dangerous value (a new and larger value of K) only at very large deformations†, the deformability increases sharply, and brittle fracture proves impossible.

In the presence of a strongly adsorption-active medium (amalgamated zinc), the size $c(\tau)$ of the incipient micro-cracks increases for the same value of τ, and the level of dangerous normal stress $P_c(c)$ falls for the same value of c. According to (2), both result in a decrease in K (proportional to the square root of σ). The quantity $(p\tau)^{1/2}$ can now reach a dangerous level (a new, much lower value of K), and brittle fracture can occur, even at ordinary and elevated temperatures, during the early stages of deformation (while the shear stress is insufficient to diminish substantially the activation energy required to overcome obstacles to movement of dislocations). With further rise in temperature (in the case of zinc–mercury to ~150° at a

† It is important that the shear stress then becomes large: relaxation of deformation in homogeneities is then very rapid (the activation energy required to overcome obstacles to movement of dislocations is substantially decreased by the work done by the applied stress).

TABLE 3. Steady rate of creep of single crystals of zinc without a coating ($\dot{\varepsilon}_0$) and with a tin coating ($\dot{\varepsilon}$).[23]

Temperature °C	P, g mm^{-2}	$\dot{\varepsilon}_0$, min^{-1}	$\dot{\varepsilon}$, min^{-1}	$\dot{\varepsilon}/\dot{\varepsilon}_0$
200	76	$0.7\cdot10^{-4}$	$0.2\cdot10^{-4}$	0.3
280	51	$1.7\cdot10^{-4}$	$10\cdot10^{-4}$	6.0
350	19	$1.0\cdot10^{-4}$	$15\cdot10^{-4}$	15.0

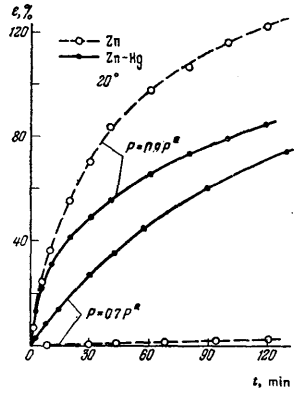


Fig. 11. Curves for the creep of single crystals of zinc at room temperature with and without a mercury coating under stresses of 0.7 and 0.9 of the yield point; $\chi_0 \sim 45°$.[24]

strain rate of $\sim 10\%$ min^{-1}), however, relaxation is already so effective and the strain-hardening factor so small that, even with a sharply reduced value of σ, the equilibrium disintegration nuclei are formed too late and are too small to become dangerous during the early stages of deformation. The value of K becomes somewhat larger again, and, owing to the very low strain-hardening factor, this new increased value is reached only after very great extension: the amalgamated crystal becomes plastic. A rough quantitative analysis has been made[15,19] of the conditions for transition from brittleness to plasticity in the absence and in the presence of a strongly adsorption-active medium; it is based on a model of the formation of dislocation pile-ups taking into accoun the obstacles to be overcome, and an expression has been obtained for the condition of deformability of a single crystal as a function of T, $\dot{\varepsilon}$, and σ. The resulting estimates for the transition temperature T_c and the transition range ΔT are fully consistent with the experimental data (see Fig. 4).

Thus, both the intrinsic and the imposed thresholds for cold-shortness are evidently of the same nature, and it is only the marked difference in the parameter σ that determines their relative positions on the temperature scale†.

The pair cadmium–gallium is of special interest in this connection, as no intrinsic threshold for cold-shortness is observed in this case.

The specific effect of the molten coating is displayed also after crossing the threshold of imposed cold-shortness (at sufficiently high temperatures or very low rates of strain) and can appear in two substantially different forms.

Thus in the case of zinc–tin[23] the presence of a molten coating is found to increase appreciably very low rates of creep of $\sim 10^{-4}$ min^{-1} (see Table 3), this softening effect being similar to the analogous action of organic surface-active media (see above); under other conditions of deformation it is masked by the effect of embrittlement. A similar phenomenon is observed at low rates of creep in the case of zinc–mercury[24] (Fig. 11).

At rather greater rates of creep (as before, in the absence of embrittlement), mercury has a hardening effect on single crystals of zinc, and raises the strain-hardening factor (Fig. 11). Such an effect is obviously connected with the normal alloying action of mercury, and for a given rate of deformation has its own upper temperature limit (determined by the activation energy for the interaction of dislocations in zinc with mercury atoms); hence at a given temperature the hardening effect is observable only when the rate of strain is not too low: in the contrary case, the softening effect predominates.

The alloying action of mercury on single crystals of zinc also appears to some extent below the threshold of imposed cold-shortness (in this case increase in the strain-hardening factor merely contributes to the development of the embrittlement). The hardening action of mercury is observed particularly clearly at low temperatures, however, when the coating is solid and adsorption effects vanish[19,42].

5

Rebinder has shown that, when there is a very marked reduction in the free surface energy of a solid with a low true solubility in a given medium, spontaneous dispersion into particles of colloidal dimensions $\delta_m = 10^{-6}$ cm, i.e. of the same order of size as the structural micro-blocks, may be detected. Development of these ideas shows that the magnitude of σ must be diminished to a few ergs of a few tenths of an erg per cm^2, and then the increase in free energy of the system due to the creation of a large area of new surface may be balanced by the gain in configurational entropy of the system[13,14]†. Kinetic and thermodynamic criteria are given for the spontaneous dispersion of a solid, and the process is shown to be considerably facilitated (to require a smaller decrease in σ) if account is taken of the free energy of the internal interfaces in the solid in its original state — the elastic energy of the sub-boundaries (dislocation lattices) and other structural defects.

Let us consider a body with a linear dimension L. Neglecting small numerical coefficients, we find its surface area to be $A_0 \sim L^2$ and its volume $V_0 \sim L^3$. The total number of micro-blocks in the surface is roughly L^2/δ_m^2, and the

† Evidently the alloying action of mercury is an additional factor. On passing from room to elevated temperatures the strain-hardening factor of amalgamated single crystals falls considerably more slowly than that of non-amalgamated crystals. This in turn contributes to the embrittling action of the coating.

† Voner's papers[62] in the theory of lyophilic colloids are of interest in this connection. He analyses (for the case of emulsions) the possibility of forming thermodynamically stable colloidal systems at extremely low values of the interfacial energy.

probability of detaching any of them is proportional to $\nu \exp(-U_A/kT)$, where U_A is the activation energy of the process and ν the thermal-vibration frequency of the block.

During one second $q \simeq (L^2/\delta_m^2)\,\nu \exp(-U_A/kT)$ particles leave the surface. Let us assume arbitrarily that the solid is able to disperse if its comminution is completed in time $t^* \simeq 1$ year $= 3 \times 10^7$ sec. The mean number of particles leaving per second should then be $q^* \simeq L^3/\delta_m^3 t^*$.

The probability of the dispersion process, or more exactly a "measure of the dispersibility of the solid", may then be defined as the ratio

$$M_D = q/q^* = (\nu t^* \delta_m / L) \times \exp(-U_A/kT).$$

A tendency to dispersion obviously corresponds to the condition $M_D \geqslant 1$ or, what is the same, the condition $\mathrm{Di} \leqslant 1$, where the dimensionless quantity Di is

$$\mathrm{Di} = U_A/kT \ln(\nu t^* \delta_m / L). \qquad (4)$$

The activation energy U_A of the process is in general defined as the work of formation of the new surface minus, firstly, the work done by external forces (or internal elastic fields due to local concentrations of stress around defects) and, secondly, the term $T\Delta S$, where ΔS is the increase in entropy of a particle on passing into the colloidal solution. Let us suppose, however, that dispersion is occurring in the absence of external forces (spontaneously); let us neglect also the work of the internal elastic fields and the gain in entropy, which leads to an overestimate of the quantity U_A, which may be written in this case in the form $U_A \sim \sigma\delta_m^2$. The condition for spontaneous dispersion is then approximately

$$\mathrm{Di}_0 = \sigma\delta_m^2/kT \ln(\nu t^* \delta_m / L) \leqslant 1. \qquad (5)$$

It is not difficult to estimate the logarithmic term in the denominator on the basis of the following considerations. The vibration frequency ν is determined by the order of magnitude of the dimension δ_m and the velocity of sound c_{sd}: $\nu \sim c_{sd}/\delta_m$. Hence

$$\ln(\nu t^* \delta_m/L) = \ln(c_{sd} t^*/L) = \ln(10^5 \times 3 \times 10^7/1) \simeq 30^{13}.$$

Choice of the numerical value of t^* is obviously not very critical, and the same applies to the quantity L.

At room temperature Eqn. (5) leads to the condition $\sigma \leqslant 4 \times 10^{-14} \times 30/\delta_m^2$, or more roughly $\sigma \leqslant 10^{-12}/\delta_m^2$ erg cm^{-2}. This means that, in the sense we have adopted, a solid can disperse into particles with $\delta_m \sim 10^{-6}$ cm if σ is reduced to 1 erg cm^{-2} or below.

The above condition, however, relates to the kinetics of the process only if it is thermodynamically possible: if the process of dispersion is thermodynamically advantageous, it will occur sufficiently rapidly provided that the inequality (5) is satisfied.

Let us now examine qualitatively the change ΔF in the free energy of the system when a solid is dispersed in a liquid into particles of colloidal dimensions: $\Delta F = \sigma\Delta A - T\Delta S$, where ΔA is the increase in free surface area of the particles and ΔS the increase in entropy of the system. Neglecting, as before, small numerical coefficients, we can write ΔA in the form $\Delta A \sim n\delta_m^2$, where $n \doteq V_0/\delta_m^3$ is the number of colloidal particles in the solution.

Let N_1 moles of the solid be dissolved in N_2 moles of liquid, when the entropy of mixing will be

$$\Delta S = -kN_A(N_1 + N_2)\{[N_1/(N_1+N_2)] \ln[N_1/(N_1+N_2)] + [N_2/(N_1+N_2)] \ln[N_2/(N_1+N_2)]\},$$

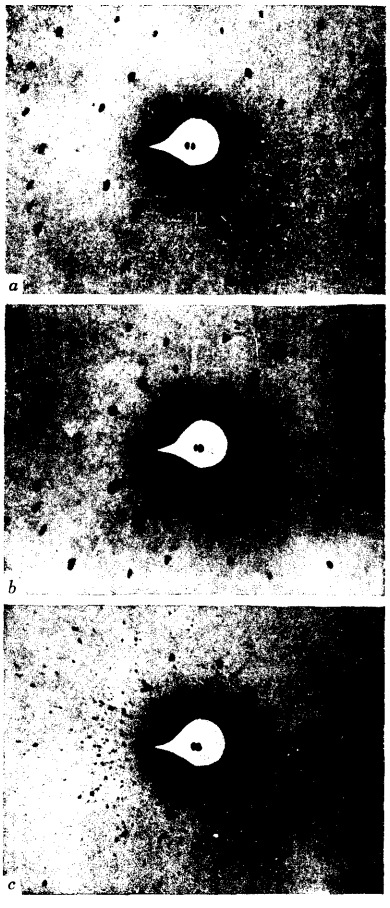


Fig. 12. Laue photographs of the same portion of a single crystal of tin: *a*) before application of coating to the specimen; *b*) 5 h after application of gallium coating; *c*) 316 h after application of gallium coating[52].

where N_A is the Avogadro number. When $N_1 \ll N_2$, we have $\Delta S = +kN_AN_1\{\ln(N_2/N_1) + 1\}$. The product N_AN_1 is in this case the number of particles n of the solid phase, and the logarithmic term is not very critical, being about 10–15. Hence $\Delta S \simeq (10 \text{ to } 15)nk$.

For the change in free energy we have $\Delta F = n\sigma\delta_m^2 - n(10 \text{ to } 15)kT$, which becomes negative if

$$\sigma \leqslant (10 \text{ to } 15) \times kT/\delta_m^2, \qquad (6)$$

giving at room temperature, approximately, $\sigma \leqslant 0.5 \times 10^{-12}/\delta_m^2$ erg cm^{-2}. Consequently in order to ensure that it is thermodynamically advantageous for dispersion into particles of $\delta_m \sim 10^{-6}$ cm to occur, the value of σ should be reduced at least to a few tenths of an erg per cm^2. The greater rigour of the resulting condition compared with criterion (4) warrants writing the latter in the approximate form (5).

Nevertheless, even the more rigorous condition (6) is still not sufficient for the process to be possible. Indeed, at extremely small values of δ_m the picture is changed sub-

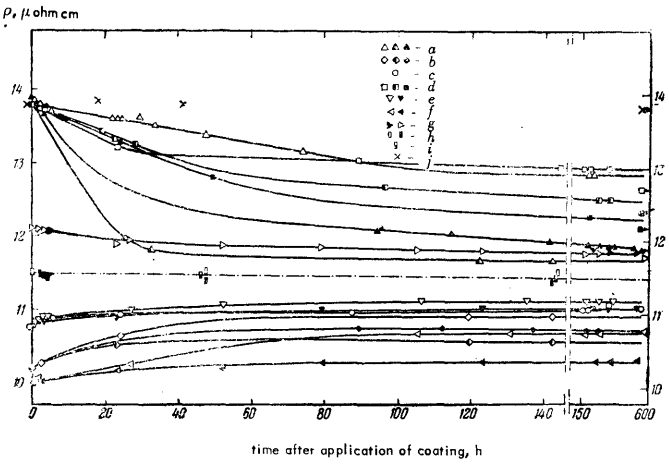


Fig. 13. Change in the electrical restivity ρ of differently oriented single crystals of tin after application of a gallium coating. Points indicated by arrows were obtained after 1800–2100 h. [52]

	Crystal	λ[001]°	Diameter, mm
a	Sn — I/1,2,3	18	0.520
b	Sn — II/1,2,3	75	0.615
c	Sn — III/3	62.5	~0.8
d	Sn — V/1,2,4	20	0.583
e	Sn — X/11,12	63	1.04
f	Sn — XI/11.12	80	1.04
g	Sn — XII/11.12	~45	1.04
h	Sn — XIII/1.2	polycrystalline	~0.6
i	Sn — XIV/5	polycrystalline	~1.0
j	Sn — V/3	20 (not coated with gallium)	0.533

Length of specimens 21 — 24 mm.

stantially if account is taken of the equilibrium between colloidal particles and the material which is in a state of true solution, as well as of the presence of a charge on the surface of the particles. As δ_m decreases, the quantity ΔF again begins to increase. It may possibly have no minimum at all, and then the colloidal state is unrealisable under the given conditions. Alternatively, in spite of the condition $\Delta F = 0$ not being satisfied, there may still be a minimum, but a positive one; then the colloidal state is metastable. Only if the condition $\Delta F = 0$ is satisfied will the quantity ΔF have a negative minimum, corresponding to a stable colloidal state, at some still smaller value of δ_m.

The microstructure of a given solid also imposes substantial restrictions on the possibility of its dispersion: the process will hardly occur at all if this structure is too coarse compared with the thermodynamically possible dimension δ_m, or if the nature of the defects between the blocks of the microstructure does not allow adsorption-active molecules to penetrate even to a small depth. In the latter case, however, it is possible to consider the successive development of the surface δ_m^2 of the particle cell by cell[63]. It must be emphasised that the microstructure of crystalline solids is a dislocation structure; its character is determined by the conditions under which the single crystal or polycrystalline aggregate was grown and by the plastic deformations which it has undergone. On the other hand, allowing for the liberation, on disintegration of the solid into colloidal particles, of the elastic energy associated with the existence of the microstructure (dislocation arrays, etc.), makes it easier to satisfy conditions (4) and (6).

Actually, in metals which have been work-hardened to the limit, the density of the dislocations may reach a value of $\sim 10^{11} - 10^{12}$ cm^{-2}, and the corresponding stored elastic energy $\sim 10^8$ ergs cm^{-3} and above. This means that every unit of the material with a linear dimension $\delta_m \sim 10^{-6}$ cm is associated with up to 10^{-10} erg. If the whole of this elastic energy could be used to produce a new surface, dispersion would prove possible even at the relatively high values of σ of ~ 10 ergs cm^{-2} and above.

The extremely interesting specific phenomena observed with the pair tin–gallium[24,64] may approach the case of a very marked diminution in σ.

Several days after application of gallium, single crystals of tin completely lose their strength and plasticity, and are easily crushed to a powder. The original spots on the Laue photographs of such specimens (in the absence of any external mechanical constraints) gradually disappear, and the picture approaches the X-ray diffraction pattern given by a polycrystal (Fig. 12), the single crystal disintegrating into individual, sharply disoriented blocks. This is supported also by measurements of the electrical resistivity of gallium-plated single crystals of tin (Fig. 13): with specimens which are oriented in such a way that their initial resistivity is low (i.e. at large angles $\lambda_{[001]}$ between the tetragonal axis and the axis of the specimen), the resistivity increases in the course of time, whereas with single crystals having a high initial resistivity (when the tetragonal axis is close to the axis of the specimen), the resistivity gradually falls after application of the coating; in both cases the resistivity tends to the value corresponding to polycrystalline tin.

At low temperatures, at which the disoriented blocks are firmly soldered together by thin layers of solidified gallium, such specimens become considerably stronger than the original material[52,64].

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PROGRESS IN METHODS FOR THE SEPARATION OF RARE-EARTH ELEMENTS

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INTRODUCTION

The position with regard to rare-earth elements (REE) has changed a good deal since our last review[1]. Experimental production of individual REE, based on Soviet raw materials, has been organised at a series of places in the USSR, and REE preparations with a very high degree of purity have become commercially available[2,3]. Work connected with the chemistry and technology of these elements has increased greatly.

In view of advances in this field which have been achieved recently in the USSR and abroad, another review of the methods for separating REE seemed timely. Not only have new, successful methods been developed — ion exchange, extraction, and electrochemical methods — but the classical methods of fractional crystallisation and fractional precipitation are also being perfected. The use of complexing agents[4] in the fractionation greatly improves these methods and makes it possible to use them industrially. A series of quite new methods of separation have been suggested: a so-called "dry" method based on differences in rates of chloride dehydration, an oxinesulphonic acid method, and others.

FRACTIONAL CRYSTALLISATION AND FRACTIONAL PRECIPITATION

In its classical form division of the total REE into subgroups by means of double sulphates is very laborious and time consuming. Complexing reagents, in particular ammonium acetate[5], have now been introduced to speed up this process. The maximum separation effect is achieved when a deficient amount of this reagent is used: the components forming more soluble double sulphates remain in solution. When separating a mixture of the yttrium-group elements to prepare 80–90% Gd and Dy concentrates, 25–30 precipitations are required instead of the 400–500 in the classical scheme. Still better results are obtained on introducing a deficient amount of a more powerful complexing agent, e.g. nitrilotriacetic acid (Complexone I), the use of which allows heavy REE, Tm, Yb, and Lu, to be isolated from a 9–10% solution in a comparatively short time.

Vagina[6], and also Gordon and Shaver[7], carried out the separation of some pairs of REE as oxalates in the presence of ethylenediaminetetraacetic acid (EDTA). When a hot solution containing oxalic acid and REE ions complexed with EDTA was slowly cooled, "homogeneous" precipitation of REE oxalates took place. The complex decomposes, to give M^{3+} ions which combine with $C_2O_4^{2-}$ ions and form difficultly soluble oxalates. The method is very selective compared with the usual oxalate method used in the absence of EDTA[8].

The same principle forms the basis of the gradual precipitation of REE by $C_2O_4^{2-}$ ions formed by hydrolysis of methyl oxalate[9]. The author considers that it does not possess any special advantage over other similar methods, but is to be recommended for purification of yttrium preparations.

Vickery[10] put forward a method of "homogeneous" precipitation of double sulphates. On adding an alkali-metal sulphite to a solution of mixed REE chlorides, soluble double sulphites are formed. By the action of oxidising agents such as O_2 or H_2O_2 in the presence of catalysts, e.g. Cu^{2+}, Mn^{2+}, Fe^{2+} (at pH 1.6–1.8), the double sulphites are gradually transformed into double sulphates. With controlled precipitation, a higher degree of separation of the total REE into subgroups is attained than is the case in the usual method employing double sulphates.

Virts[11] studied the influence of methods of crystallisation on the effectiveness of fractionation of mixtures of cerium earths in fractional crystallisation of double magnesium nitrates. The best results were obtained by seeding the hot solution of the double nitrates and allowing it to cool slowly with vigorous stirring.

Marsh[12] compared a method of crystallising basic nitrates of the type $M(NO_3)_3 . M[M(OH)_5NO_3] . 6.5H_2O$, where M = Ho, Er, or Y, with the ferricyanide method, and concluded that although the latter gives a higher separation coefficient, the nitrate method is to be preferred because of the difficulties connected with decomposing the ferricyanide and subsequently removing the iron.

A method of separating yttrium from REE using fractional crystallisation of carbonates has been described[13,14]. A solution of mixed REE nitrates was cooled to 0° and saturated with carbon dioxide. Crystalline NH_4HCO_3 was added to the mixture in amount sufficient for precipitation of 50% of the REE. The solution was stirred for three days, CO_2 was then passed for one day, and the precipitate was filtered off and dissolved in HCl. It was found that under these conditions the solubilities of the carbonates increase in the order: Pr, Nd, Sm, La, Gd, ... Lu, Y. A tenfold fractionation of a mixture containing 72 mole % Y_2O gave 98% Y_2O in 80% yield.

Marsh[15] prepared crystalline salts of REE with EDTA*, and determined their solubilities in water. The salts, made by heating the reagents,

$$M_2O_3 + 2NaOH + 2H_4E = 2Na[ME] + 5H_2O,$$

were recrystallised from weakly alkaline solution. The author considered that salts of this type are more suitable for fractional crystallisation than bromates or dimethylphosphates. Using EDTA, Marsh separated Lu and Y from a mixture.

Brunisholz et al.[16-20] recommended not only crystallisation of EDTA complexes of the type Na[ME] and NH_4[ME] with elements of the cerium group, but also fractional precipitation of the acids H[ME]. These authors isolated a

* In formulae EDTA is represented by H_4E.

series of crystalline EDTA salts of REE and determined their solubilities in water. In a study of the solubility isotherms at 0° for the system $NH_4[LaE]-NH_4[SmE]-H_2O$, it was shown that an α-phase separates, and that this consists of mixed crystals $NH_4[(Sm, La)E]$ rich in samarium, as well as a β-phase having the composition $NH_4[(La, Sm)E]$ and rich in lanthanum. When the α-phase has separated and been removed from the system, the β-phase begins to separate. It also was removed, and then a fresh portion of the mixture was added, and the crystallisation repeated. This is the basis of a cyclic process for separating REE, and the present authors have used it for fractionating mixtures containing La, Pr, Nd, and Sm.

Weaver[21] found that REE and mandelic acid give salts with formulae $M[C_8H_7O_3)_3 . nH_2O$ (n = 2.3), which differ considerably in solubility (the salts of the light metals are very soluble and those of the heavy ones sparingly so). Their solubility is greatly dependent on solution pH and temperature. The author turned this to account in fractionating an REE mixture. Mixed REE oxides (1 milligram to 100 grams) were converted to chlorides, and mandelic acid (crystalline or dissolved) or ammonium mandelate was added to their solution. The precipitates were separated and washed, then dissolved in hot dilute HCl and reprecipitated with ammonia, the resulting precipitates being combined with the appropriate filtrates and again fractionated at a definite pH. The method is recommended by the author for removing and separating heavy REE.

Freeman[22] published a preliminary communication about the application of organic solvents to the separation of mixtures of anhydrous chlorides. After a mixture of equivalent amounts of $NdCl_3$ and $DyCl_3$ had been shaken for 5 min with anhydrous acetone, 82% Nd and 18% Dy were found in the insoluble portion, and 24% Nd and 76% Dy were in solution. The method evidently deserves further development.

Indian workers[23] have suggested a method depending on the difference in the pH of precipitation of REE chromates for separating La from mixtures of elements of the cerium group not containing Ce.

Hall[24] used double chromates of the type $K_2CrO_4 . M_2(CrO_4)_3$ to separate Y from other REE. To a solution of nitrates equivalent to 100 grams of the oxides (M_2O_3 41%, Y_2O_3 58–59%), 216 grams of $K_2Cr_2O_7$ were added, the solution was made up to 1 litre and heated almost to boiling, 10% KOH solution was added dropwise with stirring, and the mixture heated for about an hour. Precipitation occurred in the order Nd, Gd(Tb), Dy, Ho, Er, and Y. The composition of the final fraction, i.e. that remaining in the mother liquor was (in %) Dy_2O_3 0.4, Ho_2O_3 0.2, Er_2O_3 0.4, and Y_2O_3 99.0.

Fractional precipitation of REE as hydroxides still remains important: it is used in work with kilogram quantities of REE. Mironov and Odnosevtsev[25,26] used it for extracting REE from industrial wastes and for obtaining concentrates of individual REE.

Trombe[27] used the ammonia method which he had worked out as long ago as 1943 to fractionate 82 kilograms of REE of the cerium group. The starting material consisted of a number of carbonates of La, Nd, Pr, Ce, Sm, and yttrium-group elements. It was dissolved in concentrated nitric acid, and the solution brought to pH 4 with ammonia (to separate Fe and Al present); then the pH was raised to 5.5 and $(NH_4)_2S_2O_8$ added to separate Ce. La was precipitated from the filtrate by passing in a mixture of gaseous ammonia and air. Precipitation was carried out in 300 litre ceramic vessels, and 4 fractions were taken: at pH 7.7, 8.1, 8.6, and finally from concentrated ammonia solution. The process was controlled by spectrophotometric and magnetic methods: 82 kilograms of mixed oxides yielded 10 kilograms of cerium oxide, 5 kilograms of oxides enriched in samarium and yttrium, 48 kilograms of mixed praseodymium and neodymium oxides, 5 kilograms of 95–97% La_2O_3, 7 kilograms of 97–98% La_2O_3, and 7 kilograms of La_2O_3 of purity greater than 99.5%.

Hilal[28] separated Ho by the ammonia method from a mixture of elements. Air containing ammonia was passed through a 4% solution of mixed nitrates, and the hydroxides were withdrawn as separate fractions. After 40 precipitations a good enrichment of holmium was attained, and there was an incidental concentration of ytterbium and yttrium. Hagiwara[29,30] carried out a series of investigations on the separation of REE mixtures as hydroxides, studying in particular the role of acidity of the medium on the process.

Misumi[31] fractionated La–Ce mixtures using urea hydrolysis at 90°–95° to effect fractional precipitation of basic salicylates and formates. He obtained cerium preparations of ~95% purity.

Kotlyarov and Kozhemyako[32] used Prandtl's method of fractional precipitation with ammonia in the presence of ammonium salts to separate La from Nd and Pr. These workers recommend a combination of fractional crystallisation with base precipitation in the presence of ammonium acetate as complexing agent for removal of small amounts of Pr in the La.

The iodate method[33,34] is often used to separate Ce from neighbouring elements. The mixture of oxides is dissolved in H_2SO_4 (1 : 1), diluted with water, and HNO_3 (specific gravity 1.42) is added, followed by H_2O_2 to convert all the cerium into the trivalent state. The whole is then left for a few minutes, cooled to 40°–60°, and NH_4IO_3 added. The reactants are well mixed and $(NH_4)_2S_2O_8$ is added to the resultant clear solution to oxidise all the cerium. Next the solution is stirred, heated to 70°–80°, and left on a hot plate for 2–3 h, after which it is stirred and cooled. A well-formed crystalline precipitate of $Ce(IO_3)_4$ forms slowly. It is separated, washed, and calcined to the oxide. The method is successful not only for the separation of cerium from REE, but also for its quantitative determination. Elements giving difficultly soluble iodates interfere: Sr, Ba, Bi, Sn, and others.

Ryabchikov and Vagina[35,36] suggest a separation of cerium from cerium-group elements, the ability of quadrivalent cerium to form complexes with acetate and oxalate ions, which are stable in solution. After using this method twice a 99% pure preparation is obtained in 96.8% yield.

EXTRACTION WITH ORGANIC SOLVENTS

The extraction method possesses a number of important advantages over crystallisation and fractional-precipitation methods: there is no need for repeated filtration or repeated dissolution of the precipitate. The time required for each separate operation is much less than for the latter two methods. Thanks to the possibility of carrying out the process continuously, it is coming into use for preparative purposes[37–41].

Thus Bock and Meyer[42] constructed a continuous countercurrent column and used it to extract quadrivalent cerium with ether. The optimum feed rate for the cerium

solution was 0.4–0.5 litres/h, while the optimum feed rate for the ether and for the wash nitric acid was 4–5 litres/h. The product contained ~99.5% Ce and the yield was 85%.

Weaver et al.[43] successfully used a countercurrent extraction method to separate large amounts of REE. In particular, this method was used to isolate more than 1 kg of 95–98% Gd_2O_3. The organic solvent used was tributylphosphate containing Varsol. The authors consider the liquid–liquid system extraction method to be the most promising for separating REE.

Fischer[44,45] used an arrangement of automatic extractors which allowed of approximately complete separation of components. Ether and pentan-2-one were the organic solvents, and $LiNO_3$ the salting-out agent. In one experiment 34 g of 90% gadolinium oxide (10% Sm and traces of Tb and Dy) gave, after putting 350 litres through a 25 stage apparatus, a 50% yield of 99% Gd_2O_3. All the samarium was removed after only 10 stages. Many more operations would be required in the crystallisation method to secure comparable results. In another extraction experiment, with an yttrium concentrate (660 g), 400 g of 99.5% Y_2O_3 were obtained after running 233 litres of pentanone through 76 stages.

The literature mentions every possible organic solvent for separating REE mixtures. To separate cerium as hexanitratoceric(IV) acid, $H_2[Ce(NO_3)_6]$, from an REE mixture, Klinaev and Senyavin[46] recommended ether, and other authors[47–50] ethyl and butyl acetates. Tributylphosphate, $(C_4H_9O)_3PO$, is widely used as a solvent[51–57]. Fomin[58] showed that from acid solution cerium goes into the organic phase as a compound of composition $Ce(NO_3)_3 \cdot 3(C_4H_9O)_3PO$. Tributylphosphate is also used to separate mixtures of light REE and to isolate yttrium.

The literature mentions[59] the use of di- and monoalkylphosphoric acids, and of a series of new trialkylphosphates, dialkylphosphates, and phosphine derivatives as solvents for REE. Peppard et al.[60,61] suggested bis(2-ethylhexyl)-orthophosphoric acid for use as the organic phase in separating tracer amounts of REE. This method is used for the separation of gadolinium. Various ketones: acetylacetone, thenoyltrifluoroacetone (TTA), pentan-2-one[62], 4-methylpentan-2-one (hexone), etc., are also widely used. As Keenan and Suttle[63] showed, when an aqueous solution of $PrCl_3$ is shaken with a benzene solution of TTA, the Pr^{3+} ions are distributed between the water and the organic phase, and form an inner complex with the TTA.

Dyrssen[64–66] made a series of studies of the extraction properties of various REE complexes, and he observed, in particular, that the oxine and cupferron complexes are extracted by chloroform and hexone. This can be used for the separation of REE mixtures. It has been mentioned that 1-nitroso-2-naphthol and disalicylalethylenediimine do not form complexes with REE, which are not therefore extracted by organic solvents in the presence of these reagents. Tropolone gives complex tropolonates with Y^{3+}, but they are difficultly soluble in chloroform.

Evidently research on the extraction method must proceed in two directions: synthesis of new complexes extractable by organic solvents, and selection of new organic solvents which can form complexes with REE, along with steady development of the extraction procedure itself.

ION EXCHANGE

The method of separation on ion-exchange columns was first suggested in 1947, and immediately became widely used. At first citric acid and its salts were exclusively used as eluents, and they are still being used for separating REE[67–70].

In 1954 Spedding and Powell[71,72] published a theory of the separation of REE citrates which was basically in agreement with a theory previously put forward by Ryabchikov[73]. Trombe and Loriers[74] made a real advance in the method of separating REE on columns. To extract REE from large volumes of eluates containing citric acid, the latter were acidified to pH < 2.7 and run through small auxiliary columns. The REE are absorbed and subsequently eluted with a small quantity of citric acid; the free citric acid can be used again. This method allows REE to be concentrated into a small volume without evaporating solutions.

To accelerate REE separation on columns the same authors[75] suggest using a series of small columns instead of one large one. The solution can be run through all the columns in succession. Before the most rapidly eluted REE component comes through, the mixture components are localised on individual columns. If the apparatus consists of a large number of columns, some of them can contain only one REE, and elution can be carried out on each column separately. The method was tested in an apparatus treating up to 1 kg of REE per cycle. At present all large-scale plants for separation usually consist of a series of columns.

In addition to citric acid, many other organic acids are at present used as eluents: lactic acid[76,77], glycolic acid[78], α-hydroxyisobutyric acid[79–81]. Mayers and Freiling[82] made a comparative study of the effectiveness of the separation of REE on Dowex 50 resin using citric, lactic, malic, and glycolic acids, as well as EDTA. The experiments were carried out at various temperatures, acidities, and complexing-agent concentrations. Of all the acids investigated the most selective was EDTA. Loriers and Carminati[83] eluted with a solution of nitrilotriacetic acid (Complexone I). Using a 130 × 3 cm Dowex 50 column and Complexone I at pH 4–6, 300–400 g of almost pure Nd, Pr, and La were obtained in one cycle. These authors also demonstrated that Complexone I is more selective than citric acid and its salts, and further that Complexone I allows more concentrated eluates to be obtained.

Holleck and Hartinger[84–86] confirmed the conclusions reached by the previous workers. On separating the same mixture under the same conditions (on Nalcite HCR), using citric acid, they isolated 44% pure Nd, whereas with Complexone I it was 83% pure.

Andreeva and Rozhdestvenskaya[87] determined the order of elution of Y when REE adsorbed on KU-2 cation-exchanger are eluted with Complexone I. The method consisted in introducing the REE mixture containing Y on to ten columns (10 × 1.8 cm) filled with the resin, and then running through an eluting solution of Complexone I until the REE appeared in the eluate from the last column. After washing the system through until there was no reaction for REE, the columns were disconnected and the REE eluted from each. It was established that, independently of the concentration and pH of the Complexone I solution, Y is washed out between Gd and the cerium REE. Using a 0.5% solution of Complexone I, pure yttrium was obtained from one concentrate containing 93% Y (remainder Dy, Tb, and Gd), and in another instance it was isolated from a concentrate containing 16.5% Y (remainder Dy, Er, and Ho).

EDTA has been more widely used as an eluent than has Complexone I. In 1953 Spedding[88] established that the preparation of individual REE can be much accelerated if the starting mixture is first fractionated with an acid ammonium salt of EDTA. The EDTA salt (pH 10) was added, in amount sufficient to form complexes with the heavy REE, to a neutral solution of 312 g of mixed oxides, and diluted with water to 90 litres. When equilibrium had been attained, the pH was adjusted to 4.5 with hydrochloric acid. After 24 h, the solution was rapidly run through a short Dowex 50 column, which was then washed with distilled water to remove all REE–EDTA complexes. The REE remaining on the resin were eluted in fractions using a solution of the calculated amount of EDTA. Pretreatment of a crude REE mixture raises the heavy REE concentration fivefold, and accelerates separation.

Achard[89] used ion-exchange columns in series to resolve mixtures of cerium earths (La, Pr, and Nd) with the aid of EDTA. Five 150 × 11 cm columns were packed with sulphonic acid cation exchanger, and a 1% EDTA solution (pH 4) used as the eluent. After passing 600 litres solution, the first column no longer contained REE, Pr was found in the second, Nd in the third and fourth, and Sm plus a small quantity of yttrium-group elements at the top of the fifth column. In a few days 600 g of crude Nd_2O_3 gave more than 200 g of Nd_2O_3 > 99.8% pure, 125 g > 99% pure, and 100 g > 98% pure.

With two columns in series packed with cation exchanger and using EDTA as the eluent, Topp[90] successfully separated a mixture of Pr, Nd, and Sm. Loriers et al.[91-93] used EDTA solution to separate Y from REE mixtures. For the separation of 200 g of mixed yttrium earths on a 150 × × 11 cm column, 125 litres of 1% sodium salt of EDTA (pH 3.5) were used for complete elution of the REE, the elements being eluted in order of decreasing atomic weight: Y was eluted between Dy and Tb. Using a more concentrated eluent solution at a higher pH, Y was eluted sooner, among elements with a higher atomic number, and this can be turned to account for isolating Y from mixtures rich in it. When EDTA is used, a three- or fourfold repetition of the operation is sufficient for the separation of a pure yttrium-group element.

To isolate Tm from an REE mixture of the yttrium group, Loriers used a mixture of EDTA and citric acid as the element. From a natural mixture containing 0.02–0.03% Tm, a product ten times richer in thulium was obtained by fractional precipitation. Separation was effected in two stages with columns in series. In the first stage EDTA at pH 4.5 was the eluent, and an Er–Yb concentrate was obtained containing 2–3% Tm. In the second stage elution was by means of a 5% citric acid solution (pH 2.7) and an 80–90% thulium concentrate was secured. The final purification was effected by elution with hot (90°) sodium citrate solution (pH 3.2), and the final product contained 99.5% Tm.

Spedding's[94,95] introduction of the Cu form of cation-exchanger resins was an important advance in the technology of REE separation. This improvement considerably increases the effectiveness of separation on ion-exchange resins. In practice separation is effected thus: one column with the resin is impregnated with the REE mixture, and the second column, more precisely its upper part*, is charged with copper. The columns are washed with distilled water to remove free ions, and then placed in series, the end of the first column being joined to the top of the second one. The columns are then eluted with EDTA solution of definite pH. The eluate (up to the time of appearance of REE ions), containing mainly $[CuE]^{2-}$, is acidified with H_2SO_4 and electrolysed to remove copper[95]. A solution containing REE then flows out; fractions of it are collected, their compositions being followed by any suitable method. The REE from the solutions are isolated as oxalates and then calcined to oxides. In this way such "difficult" mixtures as Pr and Nd can be quite successfully separated, as well as mixtures of yttrium-group elements, and the majority of REE are obtained 99.9% pure.

Many workers now use a combination of two columns[96-99], and, in particular, Noddack and Oertel[100-102] obtained pure REE on an industrial scale by this means. In four months they obtained from 96 kg of mixed starting oxides: 450 g of Lu and 2700 g of Yb, each 99.9% pure; 180 g of Tm and 1900 g of Er, each 99.6% pure; 10 500 g of Y and 3840 g of Sm 99.5% pure; and a series of other REE.

Separation was effected on a column 4 m long. The first column was made of plastic and its internal diameter was 15 cm, while the second column was of glass and had a diameter of 10 cm. Both were packed with Lewatit S-100, converted to the Na form. The first column was washed with the REE mixture to be separated and the second was converted to the Cu form. The columns were joined in series, and a 2% solution of the sodium salt of EDTA (Complexone III) was run into the first. Gradually the REE were transferred to the second column, the copper being displaced from it. After removal of all the copper, separation of fractions of REE was begun. The first stage of separation gave concentrates rich in yttrium earths, as well as pure Nd (100%) and 92% Pr (mixed with Nd and Ce). The second stage of the separation, effected with six pairs of columns each 2 m long, gave 99.0–99.9% pure preparations. The third stage was carried out when particularly pure salts were required.

Wolf and Massone[103-105] recommend the use of 2-hydroxyethyliminodiacetic acid for rapid separation of La in kilogram quantities. For example, separation of La from a mixture consisting of 86.2% La_2O_3, 6.9% CeO_2, 2.0% Pr_2O_3, 4.2% Nd_2O_3, 0.7% Sm_2O_3, and traces of yttrium earths was carried out thus: the starting mixture was converted to chlorides and run through a column (57 × 2 cm) in the upper part of which the REE were adsorbed, the resin in the lower part being in the H or Cu form (particle size 0.2–0.4 mm). The second column was charged with the H form of the same cation exchanger. Elution with a 4% solution of the hydroxyethyliminodiacetic acid was begun at 70°. With an elution rate of 0.7 cm/min, all the REE save La were concentrated in a volume of 3.7 litres of eluate. The La remaining on the column was extracted with a 4% Complexone III solution containing 2% NH_4Cl, along with NH_4OH added to bring it to pH 9. At this stage of the separation the column heating was switched off. With an elution rate of 1.5–2.0 cm/min, all the La went into 1.8 litres of eluate. By this method it was possible to separate 15.1 g of La_2O_3 in 95% yield and 99.5% purity, in 35 h. The method is recommended for separating La on a semi-industrial scale.

As well as 2-hydroxyethyliminodiacetic acid, *o*-hydroxycyclohexyliminodiacetic acid has been tried as an eluent[106]. Compared with other Complexones, these acids and their REE compounds are more soluble in water and do not give precipitates on the columns. They can give both cationic

* The reader is advised to consult ref. 95 (Ed. of Translation).

and anionic complexes with REE, the cationic ones being the more stable.

James and Bryan[107] found that thenoyltrifluoroacetone (TAA), usually used for separation of REE mixtures by the extraction method, can be employed as an eluent in separating REE mixtures on ion-exchange resins. Since TTA has a low solubility in water, a solution of it in water–dioxane is used. TTA rapidly elutes REE from the column and is recommended for separating short-lived isotopes. The method has been used for an Eu–Y mixture.

Okabe's method of separating cerium[108] is somewhat unique. The author made use of the ability of Ce(IV) to form basic salts which do not dissociate and which are not adsorbed by cation exchangers. When a solution of $Ce(NO_3)_4$ with other REE was run through an Amberlite IR-120 (NH_4 form) column, a solution of Ce(IV) free from other REE was immediately obtained. The effectiveness of the separation was greater, the higher the solution pH, while the magnitude of the flow rate affected separation but little.

A method of separating REE has been worked out[109,110] which is based on differences in rates of oxidation of complex sulphites of various REE, followed by adsorption of liberated REE cations on an ion-exchange resin.

When sulphur dioxide is passed through an aqueous suspension of REE oxides, hydroxides, or carbonates, they dissolve to give complex ions $[M(SO_3)_3]^{3-}$, stable at pH 5.5-6.1. These complex ions are oxidised by oxygen, in the air, when the metal complex goes over to the simple cation M^{3+}, which is adsorbed by a cation-exchanger. Fractionation is effected by a series of successive partial oxidations and absorptions by the resin. REE adsorbed by the resin are eluted with EDTA solution, the heavy REE being first displaced. According to the author, this method gives much purer products than the usual ion-exchange method, large quantities of REE can be processed, and it is not limited by the exchange capacity of the resin.

To separate tracer amounts of REE obtained as fission fragments in an atomic reactor, the same eluent is employed as on a macroscale; e.g. lactic acid and its salts are much used[111-120]. Here Freiling recommends the following procedure: the irradiation products are dissolved in 6 *N* HNO_3, and 20 mg of Ce, Pr, Nd, and Sm are added to the solution to act as carriers. The REE mixture is isolated as hydroxides, washed, and dissolved in a minimum amount of concentrated $HClO_4$. The resultant solution is passed through a Dowex 50 (NH_4 form) column, which is then washed with boiling distilled water. The adsorbed REE are eluted with lactic acid solutions of increasing concentration, 0.85 *N*, 0.90 *N*, 0.95 *N*, and 1 *N*, the elution temperature being 87°, and the pH 3. Freiling separated Y, Tb, Gd, Eu, Sm, Pm, Nd, and Pr quantitatively by taking fractions of the eluate. Stewart[121] suggests ammonium glycolate solution as an eluent. Elution is then effected on a column a few centimetres long and with 1 mm internal diameter, packed with Dowex 50. The eluent is a 0.25 M ammonium glycolate solution at pH 3.48. A sharp separation of Tm and Tb is obtained in 15 min on a column 3 cm long; with a 10 cm column a mixture of Lu, Tm, and Er is separated in 20 min. If the Al or Ca form of the resin is used, there is almost no separation.

Lavrukhina[122] recommended trihydroxyglutaric acid for elution of microquantities of REE. Duyckaers and Fuger[123] recommended EDTA solution. TTA is used for separating radioactive isotopes, particularly short-lived ones[107].

PAPER CHROMATOGRAPHY AND ELECTROPHORESIS

The principle of the first of these methods is based on the difference in the rates of migration of REE ions on filter paper. A drop of an aqueous solution of the REE mixture under investigation is placed at some distance from the end of a sheet of the paper which is some tens of centimetres long and a few centimetres wide. One end of the sheet is put into a vessel containing solvent and the vessel raised above the level of the bench, while the other end is put into another vessel. The solvent moves slowly in a descending stream over the paper, and the REE ions begin to migrate, different ions migrating at different rates. If the ions are quite colourless, the sheet of paper is dried, treated with a developer, and examined in daylight or by ultra-violet light, when separate coloured spots show up.

Lederer[124-131] has done the basic work in this field. He succeeded in finding conditions for identification of some REE and in separating mixtures of them. For comparison of the behaviour of a series of REE ions, a sample (sometimes 5–6 separate drops) of solution was put on a strip of Whatman No. 1 filter paper (15 × 60 cm) using a capillary tube; it formed a line 1 cm long 20 cm from the end of the strip. One end of the strip was fixed in a glass trough containing alcohol mixed with 10% of 2 *N* HCl, and the other end was put in a lower vessel. After some days the resultant chromatogram was air-dried, and then immersed in an ammonia-alcohol solution of 8-hydroxyquinoline, after which it was viewed by ultra-violet light: La, Y, Er, and Lu gave a yellow or green fluorescence, and all the other REE showed as brown or dark spots. In daylight all the spots appeared light yellow, and darkened to a brown colour after some days. Only one, Ce, five minutes after treatment with the reagent gave a brown spot.

Lederer's experiments showed that when acetone–2 *N* HCl was used as the solvent, separation took ~ 20 h. For the separation of a mixture of elements of the gadolinium group, ethanol mixed with 2 *N* HCl and NH_4SCN was used as the solvent, and an ammoniacal alcoholic solution of 8-hydroxyquinoline as developer. A mixture of Nd, Sm, and Eu, and also one of Eu and Yb, were completely separated in 48 h. The spots of Eu, Gd, and Tb partly overlapped.

A filter paper impregnated with a colloidal mass of the cation-exchange resin Dowex 50 (NH_4 form) was also used for chromatographing a mixture of La, Ce, and Y, 3% ammonium citrate solution being used as the solvent, and, as before, the spots were made visible by means of an ammonia-alcohol solution of 8-hydroxyquinoline. Spots corresponding to the La, Y, and Ce showed up.

To speed up the separation of a mixture of macroquantities of REE, Lederer developed the method of continuous paper electrophoresis. The ends of a sheet of paper carrying a drop of the mixture under investigation are placed in a solution of an electrolyte, and a direct current passed. With 300 V and a current of approximately 10 μA separation can be effected in 45 min. As the atomic number increases so does the distance traversed by an individual ion on the paper.

Lederer considers that in some cases electrophoresis is better than ion exchange or fractional crystallisation. However, in view of the small amount used, the method cannot be used for preparative work, but it is useful for effecting quicker analysis.

Moeller et al.[132] chromatographed a mixture of Y and Gd

acetylacetonates on columns packed with hydrated and anhydrous D-lactose*. The eluent was a mixture of benzene and petrol ether. Mixtures of complexes were partly resolved into optically active fractions.

METHOD BASED ON DIFFERENCES IN RATES OF ION MIGRATION

A solvent in a glass tube moves against a stream of ions at a rate greater than that of the less mobile ions, which are thus held back; the more mobile ones, however, are faster than the solvent stream and can move against it[133]. When an electric field is applied, the least mobile ions collect in the anode space and the most mobile ones in the cathode space. Convection currents, which may arise during the electrolysis, are prevented by inserting a large number of dialysis paper diaphragms into the separation tube.

Quantitative separation of La from Nd and Sm, and of Pr from Sm, was attained with a tube 40 cm long (with 105 diaphragms), at 600 V and 130 ± 10 mA, a countercurrent rate of 55 ml/h, and solution concentration 0.15–0.18 N (with respect to M^{3+}). Separation of a mixture of Pr and Nd at 60° was effected in a tube 100 cm long (having 245 diaphragms), using a 2300 V field, a 105 mA current, solution concentration (with respect to M^{3+}) 0.09 N, and a countercurrent rate of 85 ml/h. The separation took some weeks: finally the anode-space liquid contained 82% Pr and 18% Nd, and the cathode-space liquid 98% Pr (no Nd) and 2% La (?). Because the apparatus required is too complex, this method cannot in its present form be recommended for preparation of large amounts of REE.

METHODS BASED ON VALENCY CHANGES OF ELEMENTS

1. Reduction Methods

Effective methods of separating REE which can go over to the divalent state were developed long ago. However, separation of a small amount of a single element from a much larger amount of another still present difficulties, and the problem is at present under investigation. Thus Onstott[134,135] worked out an electrolytic method which allowed samarium to be freed from europium in a single operation.

The cathode was lithium amalgam, and the anode a platinum plate. Electrolysis was carried out in a 600 ml beaker with side tubes for contacts. The starting solutions were made by heating a freshly prepared mixture of Sm_2O_3 and Eu_2O_3 (98.4% and 1.6%) in 20% acetic acid, followed by addition of the hot solution to a lithium citrate solution, the pH being adjusted by adding LiOH. At the beginning of electrolysis the cathode potential was approximately -1.6 V (normal hydrogen electrode); thereafter it rose somewhat and stayed at about -2 V. The cathode current density varied from 0.0027 to 0.0162 A/cm², and experiments lasted 6 to 20 h. The Eu content was followed with the aid of the isotopes ^{152}Eu and ^{154}Eu. When electrolysis was finished the mercury phase was removed and then treated, first with water, then with dilute HNO_3. Under optimum conditions, 99.9% Eu went into the amalgam. From the solutions oxalates were precipitated, and were then calcined to the oxides. The amount of Eu was determined by its activity.

Ryabchikov et al.[136] perfected a method involving electrolytic reduction of ytterbium in the presence of citrate ions. They found that the best conditions for carrying this out were: pH 6.0, 5°, $Yb_2O_3 : K_3Cit = 1:2$, current density 0.05 A/cm², Yb concentration in the starting solution 2.0%. The method elaborated is recommended for final precipitation of ytterbium preparations from traces of neighbouring elements.

Chang[137] showed that when solutions containing mixed nitrates of Sm, Eu, and Gd, 8-hydroxyquinoline-5-sulphonic acid ("oxinesulphonic acid"), and acetic acid are electrolysed at 12 V and 0.02 A/cm² for 12 h, a greenish-yellow precipitate of composition $H_2[Eu(C_9H_5NOSO_3)_2] \cdot 4H_2O$ is formed; it is insoluble in the usual organic solvents. Spectrophotometry reveals 1–2% Sm in the precipitate, while the filtrate is free from Eu.

Achard[138*–140] suggested a new "dry" method of separating REE. When REE oxides of formula M_2O_3 are heated in vacuo with carbon, elements which can be reduced to the divalent state (Sm, Eu, and Yb) yield MO oxides which sublime owing to their higher vapour pressure.

To separate Yb, the oxide mixture is compressed with 20–30% of graphite and heated in a graphite crucible in an induction furnace. At 1400° and $< 10^{-3}$ mm Hg, YbO plus a small amount of carbon collect on a tantalum water-cooled condenser in 3 h. Three repetitions of the process separate quantitatively a mixture of Yb (52%) and La (48%). At a higher temperature (~1550°) the separation is not so good.

When YbO is heated at 1250° and $< 10^{-4}$ mm Hg in a tantalum crucible without the addition of any reducing agent, pure ytterbium metal collects on a tungsten condenser as a glistening deposit.

To separate Sm and Eu from other REE of the yttrium group, the oxides mixed with carbon are heated in a column with three graphite plates whose temperature varies from 1100° to 1600°. The deposit on the first plate consists almost entirely of SmO contaminated with traces of Eu, Yb, and Dy oxides. On the second plate there is SmO with a significant amount of Yb and traces of EuO, while on the third plate there is YbO mixed with EuO. The SmO concentrate is purified by repeated sublimation. To prepare Sm metal, the product isolated is heated at 1300°–1400° and 10^{-4} mm Hg. Pure EuO is obtained from a mixture containing Sm and Gd oxides by heating the mixture plus carbon at 1300° for 4 h; 80% of the Eu sublimes uncontaminated with other oxides.

2. Oxidation Methods

Quadrivalent cerium and ammonium oxinesulphonate give a water soluble complex[141]. This property of cerium is used to separate it from lanthanum. Oxinesulphonic acid is neutralised with excess ammonia, diluted with

* The Russian original confirmed an error which has been corrected (Ed. of Translation).

* Reference 138 appears in the authors' list of references apparently in error (Ed. of Translation).

water, and added to a mixture of cerium and lanthanum nitrates. The resultant solution is treated at 55° with a mixture of oxygen and ammonia, when Ce^{3+} is very readily oxidised to Ce^{4+}. After some hours oxidation stops and Na_2CO_3 is added. A precipitate of lanthanum carbonate forms, but the cerium stays in solution.

Misumi[142-144] worked out a method of separating praseodymium, based on its ability to undergo oxidation to the quadrivalent state when electrolysed in a melt. Praseodymium oxide containing neodymium is converted into hydroxide by fusion with KOH containing a definite amount of water. Then the melt is electrolysed at 360° in a nickel crucible, the latter being the anode and a platinum wire the cathode. The electrolytic oxidation gives a black precipitate of praseodymium oxide $PrO_{1.83}-PrO_{1.94}$* along with a small amount of hydrated neodymium oxide, and the praseodymium oxides are more than 95% pure. Repetition of the process gives a still further enriched product.

METHOD BASED ON DIFFERENCES IN RATES OF CHLORIDE DEHYDRATION

Freeman and Smith[145] found that boiling with thionyl chloride was an effective method of preparing anhydrous REE chlorides:

$$MCl_3 . xH_2O + xSOCl_2 \rightarrow MCl_3 + xSO_2 + 2xHCl.$$

Freeman published a paper[146] about experiments on separating mixtures of REE chlorides based on differences in the rate of dehydration by thionyl chloride.

A mixture of equal amounts of Nd_2O_3 and Dy_2O_3 was dissolved in hydrochloric acid, and the solution of chlorides heated with thionyl chloride; part of the chlorides become dehydrated. The mixture was then heated strongly in an argon atmosphere, and the chlorides which had not been dehydrated were converted to water insoluble oxychlorides. The anhydrous chlorides could be leached out with water: the water-soluble fraction contained 70% Nd and 30% Dy, while the residue contained 38% Nd and 62% Dy. The inventor of this method does not believe that it will find much application.

MAGNETIC METHOD

Noddack and Wicht[147-149] showed that when an REE solution flows at right angles to lines of magnetic force, fractionation of ions takes place in a way depending on their magnetic moments, the most paramagnetic ions migrating to the region of greatest field strength.

A mixed REE solution is placed in a trough provided with a capillary tube for introducing and withdrawing solution. A small platinum wire is welded to the bottom of the trough, and by heating this wire electrically, convection circulation of the liquid is brought about. The trough is put between the poles of an electromagnet for about half an hour. The effectiveness of separation depends on the circulation of solution in the vessel, degree of inhomogeneity and strength of the magnetic field, the duration of the experiment, and the initial concentration of the REE solution.

A way of separating Y from heavy REE has been elaborated, and is more effective than fractional crystallisation and fractional precipitation. The fundamental disadvantage of the method is the impossibility of working with a large amount of material.

CONCLUSION

Trials under production conditions of many methods of separation described in the literature showed that only a few of them deserve attention. It is evident that the most rational schemes of separation are those combining the most effective aspects of different methods. Ryabchikov et al.[2,3] worked out a detailed scheme for the separation of all the individual REE from a naturally-occurring mixture.

It is absolutely necessary to effect an initial separation of a mixture into cerium and yttrium groups, even if only one of the groups predominates in the mineral. It is undoubtedly easier to separate the cerium group because the series of elements which it comprises (cerium, samarium, and europium) exhibits marked variability of valency. The separation of this group is also facilitated by the absence of promethium in natural raw material. These factors make it possible to use purely chemical methods for separating the individual members of this group.

In the subsequent separation of elements it is naturally expedient to remove first the most abundant ones, cerium and lanthanum, from the mixture. Conversion of cerium to the quadrivalent state without difficulty effects its separation from adjacent elements, the mass of the starting material being reduced by about two-thirds. Lanthanum is separated from the residual mixture by crystallisation or by base precipitation, using ammonia. After that Eu and Sm are isolated by electrochemical means, and then separated.

Separation of a mixture of praseodymium and neodymium presents the greatest difficulty. Here crystallisation is not very effective, and the conversion of praseodymium into a higher valency state offers greatest promise. If it is necessary to obtain the individual REE in a highly pure state, further purification by ion-exchange and extraction methods is used.

The ytterbium group is, for a number of reasons, much harder to resolve than the cerium one. Firstly, it contains a large number of elements; secondly, these resemble one another more closely than the cerium elements do; thirdly, natural raw material always contains an excess of yttrium, an element not formally related to this group of elements but always accompanying them in nature. The old methods of separation, crystallisation, and fractional precipitation, even in conjunction with the recent improvements in them, are of little use here.

Firstly, the entire main mass of yttrium has to be removed from the mixture. This can be rapidly accomplished by treating the starting material with the calculated amount of complexing agent (EDTA) and then precipitating the elements which have not formed complexes. In this way not only is the main mass of yttrium removed, but the remaining elements are divided into small subgroups, which much facilitates separation of the mixture into its individual components. The next step is conveniently effected by ion exchange. From the last portion of the heaviest elements, ytterbium is removed electrochemically. This method gives considerably improved yields of thulium, an element of practical importance.

Now that a large number of investigators have obtained adequate amounts of very pure individual REE preparations,

* This corresponds to a mixture of $Pr_2O_3 + PrO_2$ with the latter predominating.

it can be hoped that the study of the physical and chemical properties of this large and interesting group of elements will develop much faster than has hitherto been the case.

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FORMYLATION AND ACYLATION OF ORGANIC COMPOUNDS WITH SUBSTITUTED AMIDES OF CARBOXYLIC ACIDS

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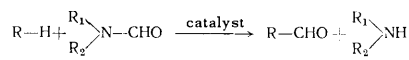
I. INTRODUCTION

The formylation of organic compounds with substituted formamides is one of the most widely used methods for the preparation of aromatic and heterocyclic aldehydes.

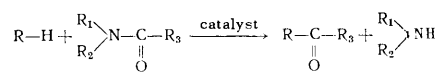
An aldehyde group can be introduced into various aromatic and heterocyclic rings by one or other of the following reactions: Gattermann[1-8], Gattermann-Koch[3-5], Karrer[6], Reimer-Tiemann[7], Duff[8,9], and some others. Although worked out in detail, they all have a rather narrow field of application. Thus. the Gattermann-Koch reaction can only be used for hydrocarbons and their halogen derivatives, the Gattermann reaction does not proceed with heterocyclic compounds (except pyrrole derivatives) and amines, and the Duff reaction is only applicable to aromatic amines and phenols. In view of the limitations of the classical synthetic methods, the new general method for preparing aromatic and heterocyclic aldehydes, using substituted formamides, is of considerable interest.

The formamide method for introducing aldehyde groups has a number of advantages over other methods of direct formylation: it can be used for preparing some dialdehydes, unsaturated aldehydes, and aromatic aminoaldehydes, and is applicable to various oxygen-, nitrogen-, sulphur-, and selenium-containing heterocyclic compounds notwithstanding their acid sensitive nature. In contrast to the Gattermann and Gattermann-Koch methods, the formylating agents used are not toxic, and the catalysts do not have dealkylating properties. The accessibility of formylating agents, the mild reaction conditions, and high yields of aldehydes make this method even more valuable.

Formylation of organic compounds with substituted formamides can be represented in its general form by the following equation:



Formylation is a particular case of the more general reaction of acylation by means of substituted acid amides:



Formylations and other acylations of organic compounds with substituted carboxylic amides were first described in the patent literature. In 1924 Fischer and his collabora-

tors[10] found that, on heating *N*-methylacetanilide with phosphorus oxychloride, a migration occurred of the acetyl group from the amino group of one ring into another aromatic ring, in the *ortho*-position to an existing substituent. Vilsmeier and Haack[11] continued the study of this reaction, and, by reacting *N*-methylformanilide with methylaniline in the presence of phosphorus oxychloride, obtained *p*-methylaminobenzaldehyde. In this way they established, in principle, the possibility of introducing an aldehyde group into an aromatic ring by reaction with a substituted formamide.

Further studies showed the formamide method to be convenient for introducing aldehyde groups into polynuclear aromatic hydrocarbons, aromatic amines, phenols, naphthols and their ethers, compounds with several functional groups, arylethylenes, and heterocyclic and some other compounds.

By this method it was possible to prepare many aldehydes otherwise difficult to obtain, for instance, indole-3-aldehyde, anthracene-9-aldehyde, picolinic aldehyde, and the aldehydes in the thiophene, selenophene, and carbazole series.

Acylation with substituted acid amides is dealt with mainly in the patent literature, and has not yet been applied to such a field of organic chemistry as has formylation. It has, nonetheless, possibilities for the synthesis of aromatic and heterocyclic ketones, especially those which cannot be obtained by the Friedel-Crafts reaction.

In this review we have undertaken to bring together the mass of disconnected information available in the literature about formylation and acylation of organic compounds by means of substituted carboxylic amides. The early work in this field has already been reviewed in the monographs by Vorozhtsov[12], Fieser and Fieser[13], and Houben-Weil[14], and also in the short surveys by Ferguson[15] and Van Dormael[16].

II. FORMYLATION OF VARIOUS ORGANIC COMPOUNDS

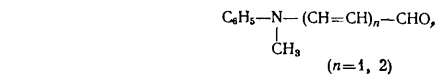
1. Reaction Conditions

Formamide and its *N*-alkyl(aryl) derivatives can be used for introducing an aldehyde group into organic compounds. The most widely used derivative is *N*-methylformanilide, as it can easily be prepared by boiling methylaniline with formic acid[17], and gives high yields of aldehydes. It has, however, lately been successfully superseded by *N*-dimethylformamide, which is a cheap industrial product[18,19].

Compared with methylformanilide, dimethylformamide requires harsher reaction conditions and as a rule gives somewhat lower yields of aldehydes[20]. On the other hand, it has a lower molecular weight and, being easily accessible, it can be used in considerable excess; it is also a good solvent and therefore improves the homogeneity of the reaction mixture.

The formylating action of diethylformamide is similar to that of dimethylformamide, while ethylformanilide acts similarly to methylformanilide[21]. Diphenylformamide has also been used in formylations[22]. Unsubstituted formamide is inactive under ordinary reaction conditions, but it yields aldehydes if $AlCl_3$ is used as a catalyst instead of phosphorus oxychloride[15,16,23,24]. It is possible that in this case a different mechanism underlies the reaction. Formyl derivatives of piperidine[25], indoline[26], and tetrahydroquinoline[27] can also be used to introduce an aldehyde group into aromatic and heterocyclic nuclei.

By using *N*-substituted methylformanilide vinylogues of the general formula



(n=1, 2)

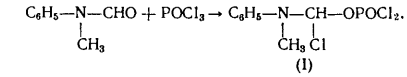
polyenal groups can be attached to aromatic compounds[28].

Phosphorus oxychloride is the most generally used condensing agent for formylations and acylations. PCl_5, $POBr_3$, oxalyl chloride, phosgene, and thionyl chloride are used much less frequently. Their action cannot be attributed to the formation of hydrogen chloride in the reaction mixture, as is borne out by the failure of dimethylformamide to formylate indole in the presence of hydrogen chloride[29].

Formylation is usually carried out by keeping the reaction mixture at 0°–40°, but sometimes heating for a short time at 100° is required. Formylation of acid sensitive heterocyclic compounds can be carried out in solution in toluene, dichloroethane, chlorobenzene, *o*-dichlorobenzene, chloroform, tetrahydrofuran, etc.

2. Reaction Mechanism

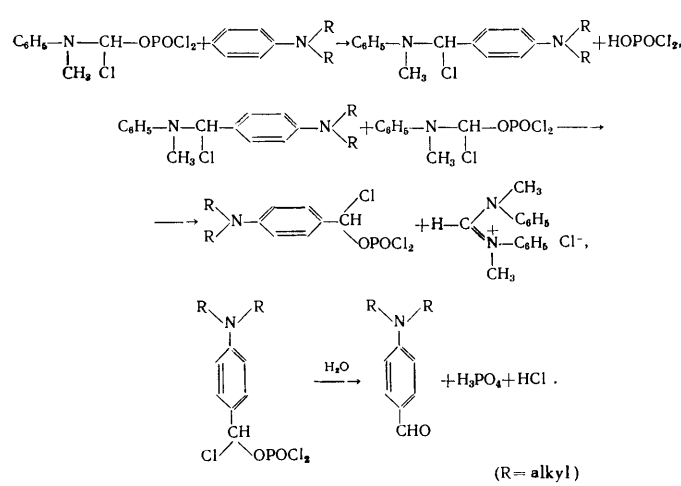
Vilsmeier and Haack[11] attempted to explain the formylation mechanism in their first paper devoted to the introduction of an aldehyde group into the nuclei of aromatic amines by the reaction with methylformanilide and phosphorus oxychloride. They thought that methylformanilide, on standing at room temperature with phosphorus oxychloride, formed product (I):



(I)

The formation of such an intermediate was confirmed in a later paper[30]. It was established that by prolonged heating at 70° this product yielded *p*-methylaminobenzaldehyde and *N*,*N*'-diphenyl-*N*,*N*'-dimethylformamidinium chloride.

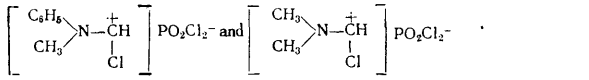
In the opinion of the authors the analogous condensation of methylformanilide with dialkylanilines proceeds in the following manner:



(R = alkyl)

The mechanism of the formylation of phenol and naphthol ethers is considered to be similar to the one above.

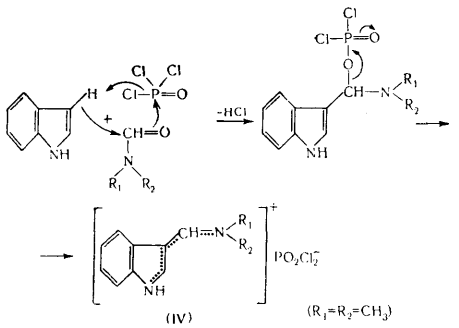
Lorenz and Wizinger[31], as well as Treibs and his collaborators[32] disputed Vilsmeier's mechanism, and ascribed a carbonium salt structure (II) and (III) to the crystalline reaction products from phosphorus oxychloride and the formylating agents:



(II) (III)

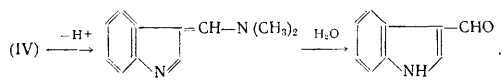
In their opinion such salts unite with the compound to be formylated, and form the products which upon decomposition by alkali yield aldehydes.

Smith[29] made a thorough study of the formylations of indole and pyrrole by means of dimethylformamide in the presence of $POCl_3$ and concluded that the reaction proceeds via the formation of intermediate quaternary ammonium salts (IV):

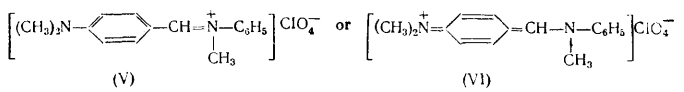


(IV) ($R_1=R_2=CH_3$)

The presence of compound (IV) in the reaction mixture was confirmed spectroscopically. This compound is completely stable in neutral and hydrochloric acid media, but loses a proton in the presence of alkali yielding 3-(dimethylaminomethylene)indolenine, which is subsequently hydrolysed quantitatively by boiling water to indole-3-aldehyde.



The intermediate formation of salt (IV) in all cases accords well with the fact that by using only catalytic quantities of $POCl_3$ very small yields of aldehydes are obtained. For complete formylation, it is necessary to use phosphorus oxychloride in quantity equivalent to that of the corresponding amide. The structure of (IV) was confirmed by spectroscopic study of the coloured reaction product from dimethylaniline, methylformanilide, and $POCl_3$.[28] This has a salt-like structure and can be isolated as a perchlorate.



(V) (VI)

By hydrolysis of the salt with dilute alkali, high yields of *p*-dimethylaminobenzaldehyde are obtained.

The formation of intermediate salts of types (IV)–(VI) is also surmised in formylations of pyrrole[34], azulene[35], and a series of other compounds. It is emphasised, however, that the role of the condensing agents lies mainly in increasing the electrophilic properties of the carbonyl carbon atom in amides.

Certain authors think that the formylation with methylformanilide is a purely ionic reaction involving the elimination of the formylium cation[33].

3. Formylation of Aromatic Hydrocarbons

Monocyclic aromatic hydrocarbons — benzene, toluene, and their homologues — do not react with *N*-alkylformanilides in the presence of the usual catalysts even at high temperatures, and can therefore be used in formylations as inert solvents.

Naphthalene and its homologues do not react, whereas anthracene, pyrene, acenaphthene, perylene, and other reactive polynuclear hydrocarbons are easy to formylate and give good yields of aldehydes. The introduction of an aldehyde group into anthracene by its reaction with methylformanilide and phosphorus oxychloride was first described in patents[36,37]. Wood and Bost[38], as well as Fieser and Hartwell[39] tested the patent data, and obtained anthracene-9-aldehyde in 92% yield. A well developed method for the preparation of this compound was described in a symposium[40]. 9-Methylanthracene[41] and anthrone[20,36] react similarly with methylformanilide. 2-Chloroanthrone and 1,5-dichloroanthracene are formylated in position 9, and simultaneously undergo chlorination by $POCl_3$ in position 10.[36]

Anthracene is more reactive than benzanthracenes. The reaction of methylformanilide with 1,2-benzanthracene is more difficult than with anthracene, whereas 1,2,5,6-dibenzanthracene does not react even after heating for 24 h, at 155°, in a sealed tube. This is explained by increased steric hindrance.

The formylation of acenaphthene and 3-methylacenaphthene gives good yields of aldehyde mixtures[41]. Acenaphthylene reacts easily with dimethylformamide in toluene solution at 100° giving 9-formylacenaphthylene, whereas under the same conditions fluoranthene does not yield an aldehyde[42]. Buu-Hoï and Lavit[42] explain the difference in the chemical behaviour of these hydrocarbons, on the basis of Thiele's theory, by the higher free valency of acenaphthene, and the position of substitution, by the maximum electron density at that point.

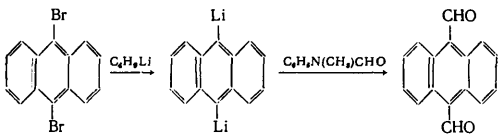
Volman et al.[43] described the preparation of pyrene-3-aldehyde by the reaction of pyrene with methylformanilide and phosphorus oxychloride. Under the same conditions dimethylformamide yields pyrene-1-aldehyde[44]. The use of *o*-dichlorobenzene as solvent is advantageous, as is shown in the formylations of benzo-[45], dibenzo-[46,47], and naphthopyrenes[48], and their homologues[46-48].

Buu-Hoï and his collaborators reported the formylations of perylene[49] and naphthacene[50] rings. As the aldehyde group is easily reducible to methyl (for instance by the Kishner method), this method may be used in the synthesis of the homologues of polynuclear hydrocarbons.

Fieser and Jones[41] showed that formylations by methylformanilide were considerably less suitable for aromatic hydrocarbons than was indicated in earlier patents. They did not succeed in obtaining the aldehydes from α-methylnaphthalene, hydrindene, phenanthrene, and chrysene by carrying out the formylation between 20° and 150°.

Attempts to prepare dialdehydes of aromatic hydrocarbons, for instance anthracene, were also unsuccessful, owing to the strong deactivating effect of the aldehyde group

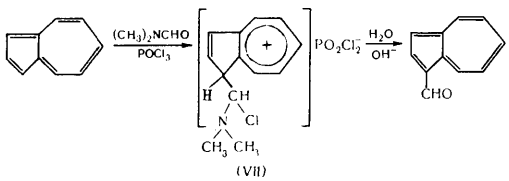
already introduced into the nucleus. If, however, the nucleophilic character of positions 9 and 10 in anthracene is enhanced by substituting the corresponding hydrogen atoms with an alkali metal, e.g. lithium, and the resulting organometallic compound is treated with methylformanilide, 9,10-dialdehyde can be obtained in about 50% yield[51]:



The mechanism of the organometallic synthesis is, naturally, completely different from the one above.

Naphthacene dialdehyde can be prepared in the usual way; 5-formyl- and 5,11-diformylnaphthacene are formed simultaneously[50].

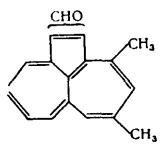
Azulene and its homologues are highly reactive to formylation. In the presence of catalysts ($POCl_3$, PCl_5, $COCl_2$, $SOCl_2$) they react with dimethylformamide yielding 1-aldehydes and 1,3-dialdehydes[34,35,52,53]. At an intermediate stage of this reaction salts of type (VII) are formed; these are hydrolysed in the presence of alkalis giving azulene aldehydes in 90–95% yield[35]:



(VII)

If the position 1 in azulene is substituted, the formyl group occupies position 3.[32]

Hafner and Schneider[54] described the formylation of 2,4-dimethyl(cyclopentadieno-1',5',4' : 1,11,10)heptalene with dimethylformamide. It is assumed that, as in the case of azulene, the aldehyde group substitutes the hydrogen atom in position 2' or 3' of the five-membered ring:



A number of workers have studied the introduction of the formyl group into the ferrocene nucleus[55–58]. The highest yield of ferrocene aldehyde (77.6%) was obtained by adding ferrocene to double the theoretical amount of a previously prepared mixture of methylformanilide and phosphorus oxychloride; the reaction mixture was left for three days, and the aldehyde isolated in the usual manner[58]:

$$(C_5H_5)_2Fe \xrightarrow[POCl_3]{C_6H_5N(CH_3)CHO} C_5H_5FeC_5H_4CHO.$$

The mild formylation conditions indicate the enhanced reactivity of ferrocene as compared with that of benzene.

Owing to the deactivation of the aldehyde group already present in the aromatic nucleus, it was for a long time impossible to introduce another such group into the ferrocene molecule even by using a considerable excess of formylating agents. Recently, however, a patent[59] described the preparation of diformylferrocene, isolated as a brownish-red oil, in small yield. The reaction was carried out at a high temperature. The acylation of ferrocene was reviewed in a paper by Nesmeyanov and Perevalova[60].

Data on the formylation of aromatic hydrocarbons are given in Table 1.

4. Formylation of Phenols, Naphthols, and Their Derivatives

Wood and Bost[38] extended the formylation by means of dimethylformanilide to ethers derived from β-naphthol.

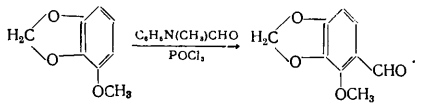
According to data published in patents[23] and journals, formylation can be applied to ethers derived from phenol[63,65], thiophenol[63], dihydric phenols[25,26,66], α- and β-naphthols[69,70], thionaphthol[72], hydroxytetralines[36,63], and their derivatives. Of special interest is the preparation of substituted hydroxyanthracene aldehydes by the formylation of 1,2- and 2,6-dimethoxyanthracenes[36].

In the preparation of alkoxyaldehydes the formyl group primarily enters the position *para* to the alkoxy group, but if that position is already occupied (for instance by a methyl group) the substitution can take place in the *o*-position, with considerably smaller yields of aldehydes.

Ethers derived from phenol (anisole and phenetole[36,63]), thymol[71], and the cresols[65] are easily formylated by different formylating agents, even after short heating of the components on a water bath in the presence of $POCl_3$, and give the corresponding alkoxybenzaldehydes in good yields.

Akabori and Senoh[25] described the preparation of veratraldehyde and 2,4-dimethoxybenzaldehyde, in which *N*-formylpiperidine was used as a formylating agent. These aldehydes were later also prepared by means of dimethylformamide[63], and methylformanilide[26].

Brownell and Weston[66] synthesised croweacin aldehyde from 1-methoxy-2,3-methylenedioxybenzene:



Ethers from α- and β-naphthols are usually formylated under milder conditions than phenolic ethers, giving higher yields of aldehydes. Buu-Hoï and his colleagues prepared a large number of alkoxy- and dialkoxynaphthalene aldehydes by formylation of the corresponding ethers with dimethylformamide[69,73–77]. Some of these aldehydes are starting materials in the synthesis of drugs used for protection against radiation sickness and for arresting the growth of sarcoma tumours. The aldehyde group was also introduced into diphenyl ether[63] and 2-hydroxynaphthalene-3-carboxylic acid[36].

All attempts to introduce two aldehyde groups into the aromatic ring of phenol and naphthol ethers failed. Negative results were also obtained in formylations of *p*-terphenyl[78], 4-chloro-2-naphthol[79], and some alkylanisoles[63].

Owing to the mild reaction conditions, formylation by means of substituted formamides can be used for introducing the aldehyde group into the nuclei of phenol[63], resorcinol[64], β-naphthol[23], and di-, tri-, and tetramethylphenols[35,65]. *p*-Hydroxybenzaldehyde was obtained in small yield, but in other cases the respective yields of aldehydes were no worse than in the Gattermann reaction. Formylation data for phenols, naphthols, the corresponding

TABLE 1. Formylation of aromatic hydrocarbons

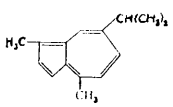
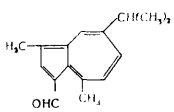
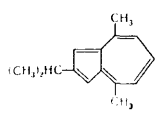
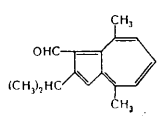
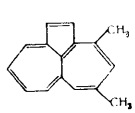
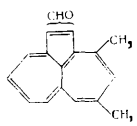
Starting material	Product	Formylating agent	Reaction conditions	Yield %	Reference
C_{10}					
Azulene	Azulene-1-aldehyde	MFA*	$POCl_3$, 24 h, 20° or 1 h, 70°	85	32
"	"	DMFA**	$POCl_3$, 5-10 min, in the cold	90-95	32, 35
"	Azulene-1,3-dialdehyde	"	$POCl_3$, 45 min, 70°	43	32
Ferrocene	Ferrocenealdehyde	MFA	$POCl_3$, 72 h, 20°-25°	77.6	57
"	"	"	$POCl_3$, 3 h, 20°	66-70	55, 56
"	Ferrocenealdehyde and bisformylferrocene	"	$POCl_3$, 15 h, 20°, or 2 h, 50°-55°	55	58
"	Ferrocenealdehyde	DMFA	$POCl_3$, 3 h, 20°	23	55
C_{11}					
1-Methylazulene	1-Methylazulene-3-aldehyde	DMFA	$POCl_3$, 5-10 min, in the cold	90-95	32, 35
C_{12}					
Acenaphthylene	Acenaphthylene-9-aldehyde	DMFA	$POCl_3$, toluene, 10 min, 100°	11-13	42
Acenaphthene	Acenaphthene-3-aldehyde	MFA	$POCl_3$, 6 days, 20°-25°	85	41
"	"	DMFA	$POCl_3$, xylene, 6 h, 100°	85	44
4,7-Dimethylazulene	4,7-Dimethylazulene-1-aldehyde	"	$POCl_3$, 5-30 min, in the cold	91	32
4,8-Dimethylazulene	4,8-Dimethylazulene-1-aldehyde	"	"	94	32
C_{13}					
3-Methylacenaphthene	A mixture of aldehydes	MFA	$POCl_3$, 6 days, 20°-25°	68	41
4,6,8-Trimethylazulene	4,6,8-Trimethylazulene-1-aldehyde	DMFA	$POCl_3$, 5-30 min, in the cold	90-95	32, 35
1,4,7-Trimethylazulene	1,4,7-Trimethylazulene-3-aldehyde	"	"	96	32
2,4,8-Trimethylazulene	2,4,8-Trimethylazulene-1-aldehyde	"	"	88	32
C_{14}					
Anthracene	Anthracene-9-aldehyde	MFA	$POCl_3$, *o*-dichlorobenzene, 20 min, 90°-95°	77-92	36-40
"	"	DMFA	$POCl_3$, 1-2 h, 100°	63	20
1,2-Benzazulene	1,2-Benzazulene-3-aldehyde	"	$POCl_3$, 5-30 min, in the cold	91	32
Anthrone	Anthrone-9-aldehyde	MFA	$POCl_3$, 1-2 h, 100°	-	20, 36
1,5-Dichloroanthracene	1,5,10-Trichloroanthracene-9-aldehyde	"	"	-	36
2-Chloroanthrone	2,10-Dichloroanthracene-9-aldehyde	"	"	-	36
C_{15}					
9-Methylanthracene	9-Methylanthracene-10-aldehyde	MFA	$POCl_3$, 45 min, 100°	84	41
Guaiazulene	Guaiazulene-3-aldehyde	MFA or DMFA	$POCl_3$, 5-30 min, in the cold	90-95	32, 35, 52
					
Isoguaiazulene	Isoguaiazulene-1-aldehyde	MFA or DMFA	$POCl_3$, 5-30 min, in the cold	88-98	32, 52
"	Isoguaiazulene-1,3-dialdehyde	"	"	96	32
Vetivazulene	Vetivazulene-1-aldehyde	"	"	up to 98	32, 52
					
2,4-Dimethyl-6-isopropylazulene	2,4-Dimethyl-6-isopropylazulene-1-aldehyde	MFA or DMFA	$POCl_3$, 5-30 min, in the cold	90	32
C_{16}					
Pyrene	Pyrene-3-aldehyde	MFA or DMFA	$POCl_3$, *o*-dichlorobenzene, 2-6 h, 100°	53	43, 44
2,4-Dimethylcyclopentadieno-(1',5',4':1,11,10)heptalene	2,4-Dimethyl-2'(or 3')-formylcyclopentadieno-(1',5',4':1,11,10)heptalene	DMFA	$POCl_3$, benzene, 1 h, 20°	57	54
					

TABLE 1 (contd.)

Starting material	Product	Formylating agent	Reaction conditions	Yield %	Reference
2-Methylguaiazulene	1,2,4-Trimethyl-2-isopropylazulene-3--aldehyde	DMFA	$POCl_3$, 5-30 min, in the cold	92	32
1-Methylvetivazulene	1,4,8-Trimethyl-2-isopropylazulene-3--aldehyde	"	"	72	32
C_{17}					
3-Methylpyrene	A mixture of aldehydes	DMFA	$POCl_3$, 6 days, 20°-25°	73	41
4-Methylpyrene	4-Methylpyrene-8-aldehyde	"	$POCl_3$, *o*-dichlorobenzene, 100°	80	61
2,3-Cyclopentenoanthracene	2,3-Cyclopenteno-9-anthraldehyde	"	$POCl_3$, toluene, 2 h, 100°	71	62
C_{18}					
1,2-Benzanthracene	1,2-Benzanthracene-10-aldehyde	DMFA	$POCl_3$, *o*-dichlorobenzene, 2 h, 95°-100°	64	39
Naphthacene	Naphthacene-5-aldehyde and naphthacene-5,11-dialdehyde	"	$POCl_3$, chlorobenzene, 6 h, 100°	-	50
C_{20}					
Perylene	Perylene-3-aldehyde	MFA	$POCl_3$, *o*-dichlorobenzene, 30 min, 95°-100°	63	49
Benzo[*cd*]pyrene	Benzo[*cd*]pyrene-3-aldehyde	"	"	90	45
C_{21}					
3-Methylperylene	3-Methylperylene-10-aldehyde	MFA	$POCl_3$, *o*-dichlorobenzene, 30 min, 95°-100°	54	49
C_{23}					
3,4,9,10-Dibenzopyrene	3,4,9,10-Dibenzopyrene-5-aldehyde	MFA	$POCl_3$, *o*-dichlorobenzene, 30 min, 95°-100°	57	50
C_{24}					
Naphtho[2,3-*a*]pyrene	Naphtho[2,3-*a*]pyrene-6-aldehyde	MFA	$POCl_3$, *o*-dichlorobenzene, 4 h, 95°-100°	51	48
"	Naphtho[2,3-*a*]pyrene-7-aldehyde	"	"	-	48
Dibenzo[*a,h*]pyrene	Dibenzo[*a,h*]pyrene-3-aldehyde	"	"	81	46
5-Methyl-dibenzo[*cd,l*]pyrene	5-Methyl-dibenzo[*cd,l*]pyrene-8-aldehyde	"	"	46	49
C_{25}					
6-Methylnaphtho[2,3-*a*]pyrene	6-Methylnaphtho[2,3-*a*]pyrene-7-aldehyde	MFA	$POCl_3$, *o*-dichlorobenzene, 4 h, 95°-100°	30	48
7-Methyldibenzo[*a,h*]pyrene	7-Methyldibenzo[*a,h*]pyrene-14-aldehyde	"	"	77	46
C_{26}					
Naphtho[2,3-*a*]naphthacene	Naptho[2,3-*a*]naphthacene-9-aldehyde	MFA	$POCl_3$, *o*-dichlorobenzene, 4 h, 95°-100°	22	50

* Methylformanilide.

** Dimethylformamide.

TABLE 2. Formylation of phenols, naphthols, and their derivatives

Starting material	Product	Formylating agent	Reaction conditions	Yield %	Reference
C_6					
Phenol	4-Hydroxybenzaldehyde	DMFA*	$POCl_3$, boiling for 2 h, 20°	low	63
Resorcinol	2,4-Dihydroxybenzaldehyde	"	"	46	64
C_7					
Anisole	Anisaldehyde	DMFA	$POCl_3$, boiling for 15 h	70	63
"	"	MFA**	$POCl_3$, 1 h, 100°	good	36
2-Chloroanisole	3-Chloro-4-methoxy-benzaldehyde	"	$POCl_3$, boiling for 15 h	3	15
Thioanisole	4-Methylthiobenzaldehyde	DMFA	$POCl_3$, boiling for 24 h	low	63

TABLE 2 (contd.)

Starting material	Product	Formylating agent	Reaction conditions	Yield %	Reference
C_8					
2,5-Dimethylphenol	4-Hydroxy-2,6-dimethylbenzaldehyde	MFA	$POCl_3$, 1 h, 100°	-	36
o-Tolyl methyl ether	4-Methoxy-3-methylbenzaldehyde	DMFA	$POCl_3$, 20°-25°	70	65
m-Tolyl methyl ether	4-Methoxy-2-methylbenzaldehyde	"	"	72	65
Phenetole	4-Ethoxybenzaldehyde	"	$POCl_3$, boiling for 15 h	70	63
Veratrole	Veratraldehyde	"	$POCl_3$, boiling for 6 h	30-40	63
"	"	MFA	$POCl_3$, room temperature	38	26
"	"	*N*-formylpiperidine	$POCl_3$, 100°	40	25
1,3-Dimethoxybenzene	2,4-Dimethoxybenzaldehyde	"	$POCl_3$, 20°-25°, then 100°	30	25
"	"	MFA	$POCl_3$, 20°-25°	85	26
1,4-Dimethoxybenzene	2,5-Dimethoxybenzaldehyde	"	"	16	26
1-Methoxy-2,3-methylenedioxybenzene	Croweacin aldehyde	"	$POCl_3$, 2 h, 100°	46	66
C_9					
3,4,5-Trimethylphenol	6-Hydroxy-2,3,4-trimethylbenzaldehyde	DMFA	$POCl_3$, 20°-25°	70	65
2,4,5-Trimethylphenol	6-Hydroxy-2,3,5-trimethylbenzaldehyde	"	"	66	65
1-Methoxy-2,5-dimethylbenzene	4-Methoxy-2,5-dimethylbenzaldehyde	"	"	72	65
1-Methoxy-2,3-dimethylbenzene	4-Methoxy-2,3-dimethylbenzaldehyde	"	"	70	67
1,2-Dimethoxy-4-methylbenzene	3,4-Dimethody-2-methylbenzaldehyde	"	$POCl_3$, boiling	35-40	63
4-Chloro-3,5-dimethylanisole	4-Chloro-3,5-dimethylanisaldehyde	MFA	$POCl_3$, 12 h, 105°	-	68
C_{10}					
2-Naphthol	2-Hydroxy-1-naphthaldehyde	MFA	$POCl_3$, 1 h, 100°	-	23, 36
2,3,4,5-Tetramethylphenol	6-Hydroxy-2,3,4,5-tetramethylbenzaldehyde	DMFA	$POCl_3$, 20°-25°	68	65
2,7-Dihydroxynaphthalene	2,7-Dihydroxy-1-naphthaldehyde	MFA	$POCl_3$, 1 h, 100°	-	36
4,8-Dihydroxynaphthalene	4,8-Dihydroxy-1-naphthaldehyde	"	"	-	36
C_{11}					
1-Methoxynaphthalene	4-Methoxy-1-naphthaldehyde	DMFA	$POCl_3$, 3 h, 95°-100°	90	69
2-Methoxynaphthalene	2-Methoxy-1-naphthaldehyde	"	"	90	69, 70
6-Methoxytetralin	6-Methoxytetralin-7-aldehyde	MFA	$POCl_3$, boiling	79	63
1-Methoxytetralin	1-Methoxytetralin-4-aldehyde	"	"	-	36
2-Methoxytetralin	2-Methoxytetralin-1-aldehyde	"	"	-	36
1-Methyl-3-methoxy-4-isopropylbenzene	3-Isopropyl-4-methoxy-6-methylbenzaldehyde	DMFA	$POCl_3$, 4 h, 30°	33-35	11
1-Methyl-2-methoxy-4-isopropylbenzene	4-Methoxy-3-methyl-6-isopropylbenzaldehyde	"	$POCl_3$, 10 h, boiling	76	63
2-Hydroxy-3-carboxynaphthalene	2-Hydroxy-3-carboxy-1-naphthaldehyde	MFA	$POCl_3$, 1 h, 100°	-	36
2-Methylthionaphthalene	2-Methylthio-1-naphthaldehyde	"	$POCl_3$, 6 h, 95-100°	35	72
C_{12}					
Phenyl ether	4-Phenoxybenzaldehyde	DMFA	$POCl_3$, boiling for 24 h	low	63
1-Methoxy-4-methylnaphthalene	1-Methoxy-4-methyl-2-naphthaldehyde	"	$POCl_3$, 3 h, 100°	22	69
2-Ethoxynaphthalene	2-Ethoxy-1-naphthaldehyde	"	$POCl_3$, 6 h, 95°-100°	74-84	36
6-Methyl-2-methoxynapthalene	2-Methoxy-6-methyl-1-naphthaldehyde	"	$POCl_3$, boiling for 5 h	86	40, 115, 73
1-Methyl-3-methoxy-4-t-butylbenzene	4-Methoxy-3-t-butyl-6-methylbenzaldehyde	"	$POCl_3$, boiling for 7 h	90	63
2,3-Dimethoxynaphthalene	2,3-Dimethoxy-1-naphthaldehyde	"	$POCl_3$, 20°-25°	23.5	74
2,7-Dimethoxynaphthalene	2,7-Dimethoxy-1-naphthaldehyde	"	$POCl_3$, 30 min, 100°	82	69
2,6-Dimethoxynaphthalene	2,6-Dimethoxy-1-naphthaldehyde	"	$POCl_3$, 3 h, 95°-100°	80	69
1,8-Dimethoxynaphthalene	4,5-Dimethoxy-1-naphthaldehyde	"	$POCl_3$, boiling in toluene	83	76
1,4-Dimethoxynaphthalene	1,4-Dimethoxy-2-naphthaldehyde	"	"	42	75
1,3-Dimethoxy-4-t-butylbenzene ether	4,6-Dimethoxy-3-t-butylbenzaldehyde	"	$POCl_3$, 6 h, 100°	79	63
C_{13}					
2-Methoxydiphenyl	4-Methoxy-3-phenylbenzaldehyde	DMFA	$POCl_3$, 90°-95°	-	63
2-Methoxy-6-ethylnaphthalene	2-Methoxy-6-ethylnaphthaldehyde	"	$POCl_3$, boiling for 5 h	98	77
2,7-Dimethoxy-1-methylnaphthalene	2,7-Dimethoxy-8-methylnaphthaldehyde	"	toluene, 9 h, 95°-100°	70	69
2,6-Dimethoxy-1-methylnaphthalene	2,6-Dimethoxy-5-methylnaphthalene-1-aldehyde	"	"	40.5	75
C_{16}					
1,2-Dimethoxyanthracene	1,2-Dimethoxy-10-chloroanthracene-9-aldehyde	MFA	toluene, 1 h, 100°	-	36
2,6-Dimethoxyanthracene	2,6-Dimethoxy-10-chloroanthracene-9-aldehyde	"	"	-	36

* Dimethylformamide.

** Methylformanilide.

ethers, and other derivatives are given in Table 2.

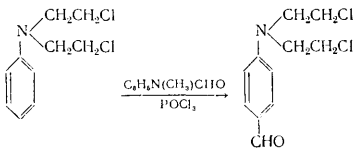
5. Formylation of Aromatic Amines

The formylation of the nucleus in aromatic amines[11] was the first example of the synthesis of aldehydes by the reaction of organic compounds with substituted formamides described in the literature.

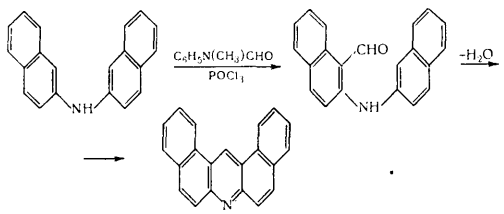
The conditions for the introduction of the aldehyde group into the nucleus of secondary and tertiary aromatic and aliphatic-aromatic amines are now well understood and the reaction is used for formylating *N*-alkyl- and *N*,*N*-dialkylanilines[11,20,80,81], toluidines[11], phenylene diamines[81], α- and β-naphthylamines[11,81], as well as diarylamines[82], and triarylamines[81,83].

Methylformanilide easily formylates dimethylaniline at 0°–10° giving 50% *p*-dimethylaminobenzaldehyde[11]. With dimethylformamide, the yield is somewhat increased, but the reaction proceeds only on heating[20].

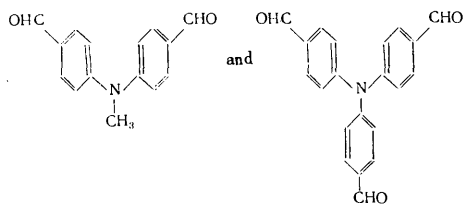
Cases have been described of the introduction of an aldehyde group into the *p*-position of secondary aliphatic-aromatic amines containing highly branched substituents, for instance diisopropylmethylaniline and isohexylaniline[84,85]. Anker and Cook[86] similarly obtained 4-(bis-β-chloroethylamino)-benzaldehyde and its derivatives:



In the nucleus of aromatic amines the formyl group usually enters the position *para* to the amino group. Recently, however, Buu-Hoï, Roger, and Hubert-Habart[87] have synthesised angular benzacridines by reacting appropriate secondary arylamines with methylformanilide. In such cases the formyl group takes up *o*-position with respect to the amino group. The aldehydes formed are thereafter easily transformed into acridines[88]:



Products containing several formyl groups were obtained by heating *N*-methyldiphenylamine and triphenylamine with dimethylformamide and $POCl_3$ (or $SOCl_2$). This reaction was described in patents[81,83]:



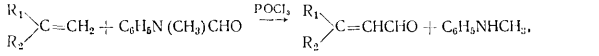
These aldehydes were used in the preparation of new styryl dyes.

The reaction of dimethylformamide with primary aromatic amines yields *N*-formanilides[89].

Data on the formylation of the aromatic ring in amines are given in Table 3.

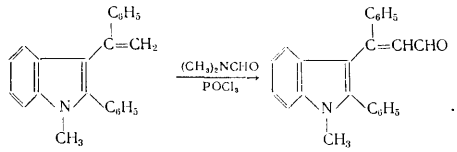
6. Preparation of Unsaturated Aldehydes and Dialdehydes

The formamide method is the only direct formylation by which α,β-unsaturated aldehydes can be prepared from substituted ethylenes[91,92]. The reaction proceeds easily without heating by mixing the unsaturated compound with methylformanilide and $POCl_3$ in solution in carbon tetrachloride, according to the equation



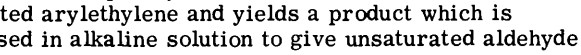
where R_1 = H, alkyl, arylmethyl, or a heterocyclic radical; R_2 = aryl.

Unsymmetrical diarylacroleins[92], which are of interest as starting materials for the synthesis of polymethine dyes, were prepared in this way. The formylation of styrene and its derivatives is carried out by heating with dimethylformamide in the presence of $POCl_3$.[93] Unsaturated aldehydes containing the indole ring can be prepared similarly.

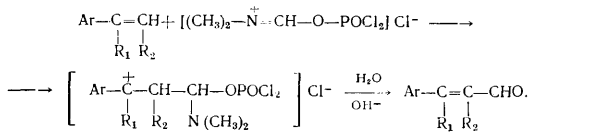


This method is of especial value for the synthesis of β-substituted cinnamaldehydes, which are not readily available and whose preparation by other methods is extremely complicated[94,95].

The authors assume that in the reaction dimethylformamide and phosphorus oxychloride form a complex salt of the following structure:



The cation subsequently reacts with the double bond in the substituted arylethylene and yields a product which is hydrolysed in alkaline solution to give unsaturated aldehyde:



Jutz[28] developed a new method for the preparation of unsaturated aldehydes by the direct introduction of the polyenal group into organic compounds. The acylating agents in this reaction are methylformanilide vinylogues: 3-(*N*-methylanilino)acrolein and 1-(*N*-methylanilino)penta-1,3-diene-5-al; the reaction is carried out with cooling in chloroform or tetrahydrofuran solution, and $POCl_3$ is used as

TABLE 3. Formylation of aromatic amines

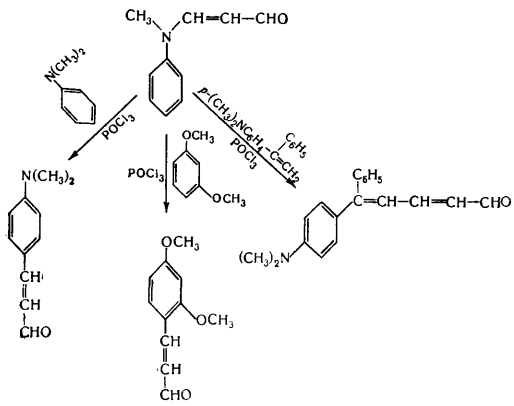
Starting material	Product	Formylating agent	Reaction conditions	Yield %	Reference
C_7					
N-Methylaniline	*p*-(Methylamino)benzaldehyde	MFA* or DMFA**	$POCl_3$, 70°	26	11
C_8					
N,*N*-Dimethylaniline	*p*-(Dimethylamino)benzaldehyde	MFA	$POCl_3$, 0°-10°	50	11, 80
"	"	DMFA	$POCl_3$, 2 h, 90°-95°	71	20, 81
C_9					
N,*N*-Dimethyl-*m*-toluidine	2-Methyl-4-(dimethylamino)benzaldehyde	DMFA	$POCl_3$, 50°	low	11
N-Methyl-*N*-(β-chloroethyl)aniline	*p*-[*N*-Methyl-*N*-(β-chloroethylamino)] benzaldehyde	"	$POCl_3$, benzene, 4 h, 30°-35°	32	86
$C_6H_5N(CH_3)CH_2CH_2Cl$	p-$OHCC_6H_4N(CH_3)CH_2CH_2Cl$				
C_{10}					
N,*N*-Diethylaniline	*p*-(Diethylamino)benzaldehyde	DMFA	$POCl_3$, 70°	-	11, 81
N,*N*,*N*',*N*'-Tetramethyl-*m*-phenylenediamine	An aldehyde, CHO position not indicated	"	$POCl_3$, 1.5 h, 95°	-	81
N-Ethyl-*N*-(β-chloroethyl) aniline	*p*-[Ethyl(β-chloroethyl) amino]benzaldehyde	MFA	$POCl_3$, benzene, 4.5 h, 30°-35°	42	86
N,*N*-Bis(β-chloroethyl)aniline	*p*-[Bis-(β-chloroethyl)amino]benzaldehyde	"	"	70	86
$C_6H_5N(CH_2CH_2Cl)_2$	p-$OHC-C_6H_4N(CH_2CH_2Cl)_2$				
C_{11}					
o-Methyl-*N*,*N*-diethylaniline	3-Methyl-4-(diethylamino)benzaldehyde	DMFA	$POCl_3$, 1.5 h, 95°	-	81
m-Methyl-*N*,*N*-diethylaniline	2-Methyl-4-(diethylamino)benzaldehyde	"	"	-	81
C_{12}					
N,*N*-Dimethyl-α-naphthylamine	4-(Dimethylamino)-1-naphthaldehyde	MFA	$POCl_3$, 50°	low	11
N-Isohexylaniline	*p*-(Isohexylamino)benzaldehyde	"	$POCl_3$, benzene, 15 h, 10°	-	84, 85
$C_6H_5N(H)-CH(CH_3)-C(CH_3)_3$	p-$OHC-C_6H_4-N(H)-CH(CH_3)-C(CH_3)_3$				
C_{13}					
N-Methyldiphenylamine	*N*-Methylbis(4-formylphenyl)amine	DMFA	$POCl_3$, 1.5 h, 90°-95°	-	83
N-Isoheptylaniline	*p*-(*N*-Isoheptylamino)benzaldehyde	MFA	$POCl_3$, benzene, 15 h, 10°	-	84, 85
$C_6H_5-NH-CH(CH(CH_3)_2)_2$					
o-Methyl(*N*-isohexylaniline	3-Methyl-4-(*N*-isohexylamino)benzaldehyde	MFA	$POCl_3$, benzene, 15 h, 10°	-	84, 85
$CH_3C_6H_3(CH_3)-NH-CH(CH_3)-C(CH_3)_2-CH_3$	$OHC-C_6H_2(CH_3)-NH-CH(CH_3)-C(CH_3)_2-CH_3$				
C_{14}					
N-Methyl-*N*-benzylaniline	*p*-(*N*-Methyl-*N*-benzylamino)benzaldehyde	MFA	$POCl_3$, benzene, 20°	82	11
N,*N*-Diethyl-1-naphthylamine	4-(*N*,*N*-Diethylamino)-1-naphthaldehyde	DMFA	$POCl_3$, 1.5 h, 95°-100°	-	81
N,*N*-Diethyl-2-naphthylamine	6-(*N*,*N*-Diethylamino)-2-naphthaldehyde	"	"	-	81
N,*N*,*N*',*N*'-Tetraethyl-*m*-phenylenediamine	An aldehyde, position of CHO group not indicated	"	"	-	81
C_{16}					
N-Phenyl-2-naphthylamine	2-Phenylamino-1-naphthaldehyde	MFA	$POCl_3$, 100°	48***	82
o-(Diethylamino)diphenyl	3-Phenyl-4-(diethylamino)benzaldehyde	DMFA	$POCl_3$, 1.5 h, 95°-100°	-	81
N,*N*'-Dimethyl-*N*,*N*'-diphenylethylenediamine	*N*,*N*'-Dimethyl-*N*,*N*'-di(*p*-formylphenyl) ethylenediamine	"	"	70	81, 90
$C_6H_5N(CH_3)-CH_2-CH_2-N(CH_3)C_6H_5$	$OHCC_6H_4N(CH_3)-CH_2-CH_2-N(CH_3)C_6H_4CHO$				
C_{18}					
Triphenylamine	Tris (*p*-formylphenyl)amine	DMFA	$POCl_3$, 1.5 h, 95°-100°	-	81, 83
N,*N*'-Diethyl-*N*,*N*'-diphenylethylenediamine	*N*,*N*'-Diethyl-*N*,*N*'-di(*p*-formylphenyl)-ethylenediamine	"	$POCl_3$, or $SOCl_2$, in the cold	-	90
$C_6H_5N(C_2H_5)-CH_2CH_2N(C_2H_5)C_6H_5$	$OHCC_6H_4N(C_2H_5)-CH_2CH_2N(C_2H_5)C_6H_4CHO$				
C_{20}					
2-Dinaphthylamine	2-Naphthylamino-1-naphthaldehyde	MFA	$POCl_3$, 100°	-	82
N,*N*-Dibenzylaniline	*p*-Dibenzylaminobenzaldehyde	"	$POCl_3$, 40°-50°	-	11

* Methylformanilide.

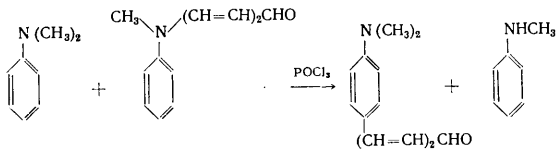
** Diethylformamide.

*** The yield was calculated from the benzacridine formed on cyclisation.

condensing agent:

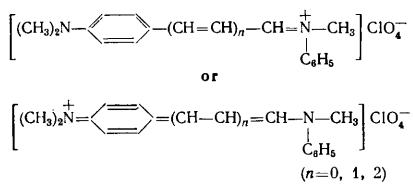


The penta-1,3-dienal radical (−CH = CH − CH = CH − CHO) can be introduced directly into the *p*-position of dimethylaniline in the following manner:



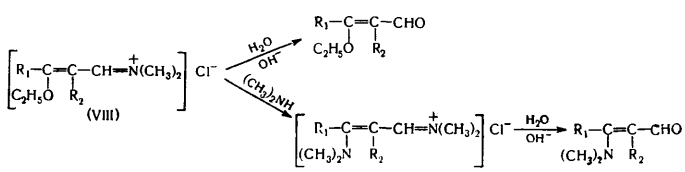
The introduction of polyenal chains into the aromatic nucleus can also be applied, as shown recently[54,96], to azulenic hydrocarbons. These reactions are a convincing example of the principle of vinylogy.

The intermediate products in this reaction are deeply coloured compounds, which can be isolated in the form of perchlorates:



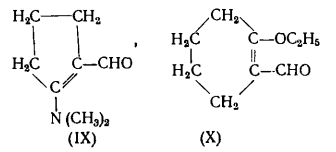
The Jutz method has obviously a wide applicability and may prove even more useful in the future.

Arnold and Zemlicka[97] studied the formylation of the diethylketals of acetone, acetophenone, propiophenone, cyclopentanone, and cyclohexanone by means of dimethylformamide in the presence of phosgene solution in dichloroethane. It is assumed that in the course of the reaction an intermediate quaternary salt (VIII) is formed, whose decomposition follows a different pattern according to the nature of the ketone and other reagents.

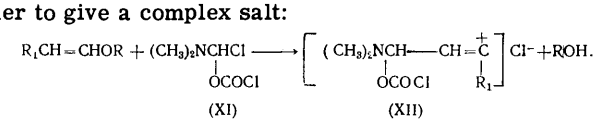


It is also highly probable that the cation of the salt (VIII) is formed as a result of the elimination of alcohol from the ketal molecule. The vinyl ether formed is subsequently formylated according to the mechanism given above.

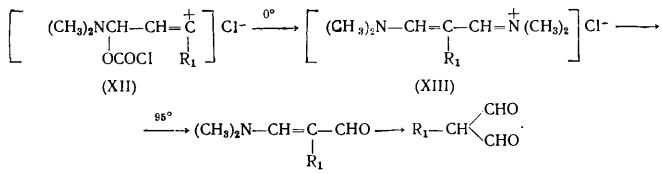
Using this method, the authors prepared various β-ethoxy(dimethylamino)acroleins in good yields. From diethylketals of cyclopentanone and cyclohexanone, 2-dimethylaminocyclopenten-1-aldehyde (IX) and 2-ethoxycyclohexan-1-aldehyde (X) are formed, respectively:



Arnold and Sorm[98]* developed a general method for the preparation of dialdehydes of the type $R-CH(CHO)_2$, by the formylation of vinyl ethers, acetals, and α-chloro-ethers with dimethylformamide and a solution of phosgene in dichloroethane. It is assumed that in the course of the reaction an intermediate product (XI) is formed from dimethylformamide and phosgene, which unites with vinyl ether to give a complex salt:



The decomposition of the complex by potassium carbonate solution at 0° results in quaternary salts, which, on further hydrolysis with aqueous alkali, are transformed into dialdehydes, according to the following scheme:



Such a reaction mechanism is confirmed to some extent by the separation and identification of the intermediate products (XI)−(XIII). The reaction of acetals and chloro-ethers with dimethylformamide apparently also proceeds via the formation of vinyl ethers. Dialdehydes of the general formula $R-CH-(CHO)_2$ were prepared by the Arnold and Sorm method, where R = H, CH_3, C_2H_5, iso-C_3H_7, C_4H_9, C_5H_{11}, C_6H_5, $C_6H_5CH_2$ (Table 4).

7. Formylation of Heterocyclic Compounds

Formylation by means of dimethylformamide and methylformanilide has lately been used with success for the preparation of a series of heterocyclic aldehydes. The application of this method to heterocyclic compounds is of special interest, as the Gattermann-Koch and Reimer-Tiemann reactions often give poor results owing to the acid sensitive character of certain heterocyclic compounds.

Heterocyclic aldehydes can be conveniently obtained by periodate oxidation of the carbon−carbon sugar derivatives with heterocyclic aglucones[99-102].

Indole-3-aldehyde was the first heterocyclic aldehyde (not counting those dealt with in patents) to be synthesised by the formanilide method[103]. This compound is the starting

* The mechanism given here is not that suggested by Arnold and Sorm, for details of which see the original paper. (Ed. of Translation.)

TABLE 4. Unsaturated aldehydes prepared by the formamide method

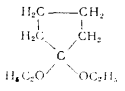
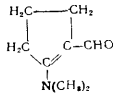
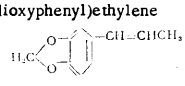
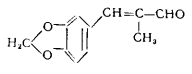
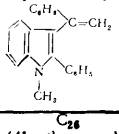
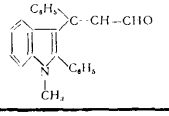
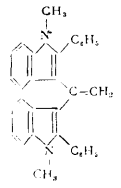
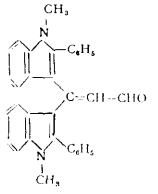
Starting material	Product	Formylating agent	Reaction conditions	Yield %	Reference
C_7					
Acetone diethylketal $CH_3C(OC_2H_5)_2CH_3$	β-dimethylaminocrotonaldehyde $CH_3-C(=CH-CHO)-N(CH_3)_2$	DMFA*	$COCl_2$, dichloroethane, 3 h, 40°	46	97
C_8					
Styrene	Cinnamaldehyde	DMFA	$POCl_3$, 1 h, 75°-80°	41	93
"	"	"	$POCl_3$, dichloroethane, boiling, 15 min	38	93
"	"	MFA**	$POCl_3$, CCl_4, 20°-25°	-	91
1,3-Dimethoxybenzene	2,4-Dimethoxycinnamaldehyde	MAPr***	$POCl_3$, $CHCl_3$, 1.5 h, 35°	90	28
Dimethylaniline	*p*-(Dimethylamino)cinnamaldehyde	"	"	70-80	28
"	1-[*p*-(Dimethylamino)phenyl]penta-1,3-dien-5-al $(CH_3)_2N-C_6H_4-(CH=CH)_2CHO$	MAPd****	"	18-20	28
Diethyl succinate	Diethyl 2-formylsuccinate	DMFA	NaH, ethanol	-	22
C_9					
4-Methylstyrene	*p*-Methylcinnamaldehyde	DMFA	$POCl_3$, dichloroethane, 40 min, 5°, or 15 min [boiling? (Ed. of Translation)]	46	93
1-Methyl-1-phenylethylene	b Phenylcrotonaldehyde	"	$POCl_3$, boiling for 1 h, 75°-80°	52	93
Cyclopentanone diethylketal 	2-Dimethylaminocyclopenten-1-aldehyde 	"	$COCl_2$, dichloroethane, 3 h, 40°	47.6	97
Pinacolone diethylketal	β-Butyl-β-ethoxyacrolein	DMFA	$COCl_2$, dichlorethane, 3 h, 40°	82	97
C_{10}					
Azulene	1-(Azulenyl-1')prop-1-en-3-al	MAPr	$POCl_3$, 20°-25°	good	96
"	1-(Azulenyl-1')penta-1,3-dien-5-al	MAPd	"	"	96
1-Methyl-1-(*p*-methylphenyl)-ethylene	β-(4'-Methylphenyl)crotonaldehyde	DMFA	$POCl_3$, 1 h, 75°-80°	64	93
1-Methyl-2-(*p*-methoxyphenyl)-ethylene	α-Methyl-β-(4'-methoxyphenyl)acrolein	"	"	68	93
1-Methyl-2-(methylene-3',4'-dioxyphenyl)ethylene 	α-Methyl-β-(methylene-3',4'-dioxyphenyl)-acrolein 	"	"	27	93
Cyclohexanone diethylketal	2-Ethoxycyclohexen-1-aldehyde	DMFA	$COCl_2$, dichloroethane, 3 h, 40°	59	97
Diethylaniline	4-Dimethylaminocinnamaldehyde	MAPr	$POCl_3$, $CHCl_3$, 1.5 h, 35°	84	28
C_{12}					
1-Methyl-1-(*p*-isopropylphenyl)-ethylene	β-(*p*-Isopropylphenyl)crotonaldehyde	DMFA	$POCl_3$, dichloroethane, 15 min boiling	34	93
Acetophenone diethylketal	β-Chlorocinnamaldehyde and β-dimethylaminocinnamaldehyde	"	$COCl_2$, dichloroethane, 3 h, 40°	5.8 and 25.7	97
C_{13}					
Propiophenone diethylketal	α-Methyl-β-ethoxy-β-phenylacrolein	DMFA	$COCl_2$, dichloroethane, 3 h, 40°	92	97
C_{14}					
1,1-Bis(*p*-hydroxyphenyl)ethylene	β,β-Bis(*p*-hydroxyphenyl)acrolein	MFA	$POCl_3$, CCl_4, 20°	-	91
1,1-Bis(*p*-chlorophenyl)ethylene	β,β-Bis(*p*'-chlorophenyl)acrolein	"	"	-	91
C_{15}					
Guaiazulene	1-(Guaiazulenyl-3')prop-1-en-3-al	MAPr	$POCl_3$, $CHCl_3$, 1.5 h, 35°	good	96
"	1-(Guaiazulenyl-3')penta-1,3-dien-5-al	MAPd	"	-	96
C_{16}					
1-Phenyl-1-(*p*-dimethylamino-phenyl)-ethylene	1-Phenyl-1-(*p*-dimethylaminophenyl)-penta-1,3-dien-5-al	MAPd	$POCl_3$, $CHCl_3$, 1.5 h, 35°	94	28
1,1-Bis-(*p*-methylaminophenyl)-ethylene	β,β-Bis(*p*-dimethylaminophenyl) acrolein	MFA	$POCl_3$, CCl_4, room temperature	-	91

TABLE 4. (contd.)

Starting material	Product	Formylating agent	Reaction conditions	Yield %	Reference
C_{23} 1-Phenyl-1-(1'-methyl-2'-phenylindol-3'-yl)ethylene	β-Phenyl-β-(1-methylphenylindolyl-3')-acrolein	MFA	$POCl_3$, CCl_4, room temperature	-	91
1-(*p*-Chlorophenyl)-1-(1'-methyl-2'-phenylindol-3'-yl)ethylene 	β-(*p*-Chlorophenyl)-β-(1'-methyl-2'-phenylindol-3'-yl)acrolein 	MFA	$POCl_3$, CCl_4, room temperature	-	91
C_{26} 1,1-Bis(4'-ethoxynaphth-1'-yl)-ethylene	β,β-Bis(4-ethoxynaphth-1-yl)acrolein	MFA		-	91
C_{32} 1,1-Bis(1'-methyl-2'-phenyl-indolyl-3')ethylene 	2,2-Bis(1'-methyl-2'-phenylindolyl-3')-acrolein 	MFA	$POCl_3$, CCl_4, room temperature	-	91

* Dimethylformamide.

** Methylformanilide.

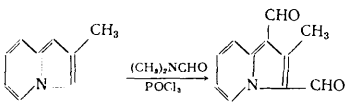
*** 2-*Phenylmethylamino*acrolein.

**** 5-Phenylmethylaminopenta-1, 3-dien-5-al.

material in the synthesis of racemic tryptophan. It can be prepared by direct formylation of indole or its potassium salt in 53–72% yield[103,104], or by formylation of 2-ethoxycarbonyl indole; in the latter case the aldehyde separates in quantitative yield after saponification and decarboxylation[103]. In some later work dimethylformamide is given preference over methylformanilide, as it can serve at the same time as a solvent[29,105]. This last method, which gives quantitative yields, is considered the best for the preparation of indole-3-aldehyde.

Pyrrole reacts with dimethylformamide even in the cold, forming 83% of pyrrole-2-aldehyde[29]. Other aldehydes of the pyrrole series are obtained in the like manner[106].

Holland and Nayler[107] established that the formylation of 2-methylpyrrocoline by this method yields a product with two aldehyde groups in the nucleus:



Buu-Hoi and Hoan[108] extended the formylation by methylformanilide to carbazoles, and described the preparation of a series of *N*-alkylcarbazole-3-aldehydes. Kucherova et al.[109] found that the formylation of *N*-substituted 1,2,3,4-tetrahydrocarbazoles, in contrast to that of *N*-alkylcarbazoles, yields 7-aldehydes.

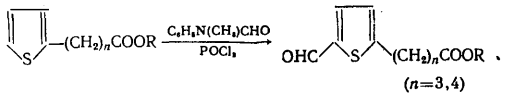
Of special interest is the first direct formylation of the pyridine ring by methylformanilide[110], in which an α-aldehyde, but not the β-isomer, was obtained. Quinoline does not react at all, whereas *N*-methyl-1,2,3,4-tetrahydroquinoline is formylated yielding 46% of the 6-aldehyde[111]. Attempts to formylate pyrazole and *N*-benzoylpyrazole were not successful[112,113], but nevertheless Finar and Lord recently carried out the formylation of 1-methyl-, 1-phenyl-, and 1-*m*-nitrophenylpyrazoles, and some other derivatives, with dimethylformamide, and obtained 4-aldehydes[114].

The formylation of oxygen-containing acid sensitive heterocycles by means of dimethylformamide has recently been reported to be successful. The formylation of furan and its homologues with dimethylformamide in the presence of $POCl_3$ is worthy of mention[115]. Yields of α-aldehydes are 50–70%. Harsher reaction conditions are required for the introduction of an aldehyde group into a benzofuran ring, and the yields are lower than in the case of furan and its derivatives[116,117]. A 7-methoxy substituent has a beneficial effect, whereas a chlorine atom in position 5 inhibits the formylation[116]. 2-Methoxydibenzofuran[118], 5-ethylnaphtho[2,1-*b*]furan[116], and phenanthro[3,2-*a*]dibenzofuran[119] have also been formylated. The formylation of certain hydroxycoumarins[120] and 1,4-dioxane[121] has been studied.

The formylation of thiophene and its derivatives has been studied in detail by a number of workers. King and Nord[122,123] found that at 90°–100° the aldehyde group enters the α-position. If both α-positions are occupied, the formyl group is attached in the β-position, so that even 2,3,5-trimethylthiophene forms an aldehyde in satisfactory yield. The formylation of thiophene with dimethylformamide can also be carried out at higher temperatures[20,124,125], but Weston and Michaelis[21] found that on increasing the reaction time to 16–18 h, the reaction is completed even at room temperature. As expected, attempts at further formylation of thiophene aldehyde to obtain dialdehydes, proved unsuccessful.

The formylation of alkyl-[20,21,122-128] and aryl-[129] thiophenes has been the most thoroughly studied synthesis of heterocyclic aldehydes by means of substituted formamides. In the formylation of 5-bromothiophene an exchange of halogen atoms takes place between that compound and $POCl_3$, giving rise to 5-chlorothiophene-2-aldehyde. 5-Bromothiophene-2-aldehyde is obtained if $POBr_3$ is used in the reaction instead of $POCl_3$.[123]

Gol'dfarb and his colleagues described the preparation of new aldehydes derived from thiophene and bis(2-thienyl)-methane, which were subsequently used for the synthesis of aliphatic alcohols[128,130-132]. Esters of thiophene-2-carboxylic acids are formylated in a similar manner[133,134]:



Weston and Michaelis[21] also described the introduction of an aldehyde group into thionaphthene ring. Their results in the preparation of thionaphthene-3-aldehyde were recently confirmed by Gnaisas[135]. In contrast to thionaphthene, 4,5,6,7-tetrahydrothionaphthene yields a 2-aldehyde[136].

The first report on the formylation of the selenophene ring in 3,5-diarylselenophenes was published in 1954[129]. Yur'ev and his associates obtained high yields of selenophene-2-aldehyde and its homologues by this method[137-139].

Cauquil and Casadevall[140] developed a method for the preparation of phenothiazine aldehydes. On formylating unsubstituted phenothiazine or *N*-acylphenothiazine, the *N*-formyl derivatives are formed, whereas *N*-alkylphenothiazines yield phenothiazine-3-aldehydes. If the positions 3 and 4 are occupied, no formylation takes place.

Data available in the literature on the formylation of heterocyclic compounds with substituted formamides are collected in Table 5.

TABLE 5. Formylation of heterocyclic compounds

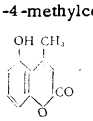
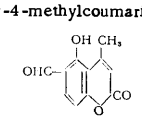
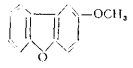
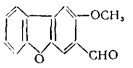
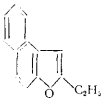
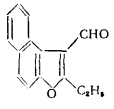
Starting material	Product	Formylating agent	Reaction conditions	Yield %	Reference
	1. Oxygen-containing heterocycles				
C_4					
Furan	Furfural	DMFA*	$POCl_3$, 30 min, 100°	64	115
1,4-Dioxane	1,4-Dioxane-2-aldehyde	MFA**	$POCl_3$, heat	37	121
C_5					
2-Methylfuran	5-Methylfurfural	DMFA	$POCl_3$, 30 min, 100°	76	115
C_6					
2-Ethylfuran	5-Ethylfurfural	DMFA	$POCl_3$, 30 min, 100°	50	115
2,5-Dimethylfuran	No aldehyde is formed	"	"	-	115
C_8					
Benzofuran	Benzofuran-2-aldehyde	DMFA	$POCl_3$, boiling for 6-7 h	37.7	116
C_9					
2-Methylbenzofuran	2-Methylbenzofuran-3-aldehyde	DMFA	$POCl_3$, boiling for 11 h	75	116
C_{10}					
2-Ethylbenzofuran	2-Ethylbenzofuran-3-aldehyde	DMFA	$POCl_3$, boiling for 11 h	66	116
2-Ethyl-5-chlorobenzofuran	2-Ethyl-5-chlorobenzofuran-3-aldehyde	"	"	6	116
5-Hydroxy-4-methylcoumarin	5-Hydroxy-4-methylcoumarin-6-aldehyde	MFA	"	low	120
					
2,7-Dihydroxy-4-methylcoumarin	7,9-Dihydroxy-4-methylcoumarin-8-aldehyde	MFA	$POCl_3$, boiling for 11 h	good	121
C_{11}					
2-Ethyl-7-methoxybenzofuran	2-Ethyl-7-methoxybenzofuran-3-aldehyde	DMFA	$POCl_3$, boiling for 11 h	76	116
4,7-Dimethyl-5-hydroxycoumarin	4,7-Dimethyl-5-hydroxycoumarin-8-aldehyde and 4,7-dimethyl-5-hydroxycoumarin-6-aldehyde	MFA	"	- -	120 120

TABLE 5. (contd.)

Starting material	Product	Formylating agent	Reaction conditions	Yield %	Reference
C_{12}					
5,7-Dimethoxy-4-methylcoumarin	5,7-Dimethoxy-4-methylcoumarin-6-aldehyde and 5,7-dimethoxy-4-methylcoumarin-8-aldehyde	MFA	$POCl_3$, boiling for 11 h	low "	121 121
C_{13}					
2-Methoxybenzofuran 	2-Methoxybenzofuran-3-aldehyde 	DMFA	$POCl_3$, 6 h, 95°-100°	25	118
5,6,7-Trimethoxy-4-methylcoumarin	5,6,7-Trimethoxy-4-methylcoumarin-8-aldehyde	MFA	$POCl_3$, 6 h, 95°-100°	low	120
C_{14}					
2-Phenylbenzofuran	2-Phenylbenzofuran-3-aldehyde	DMFA	$POCl_3$, 8 h	good	117
5-Ethyl-(2',1':2,3)napthofuran 	5-Ethyl-(2',1':2,3)naphthofuran-4-aldehyde 	"	$POCl_3$, toluene, boiling for 11 h	49.5	116
C_{15}					
2-Benzylbenzofuran	2-Benzylfuran-3-aldehyde	DMFA	$POCl_3$, 8 h	good	117
3-Benzylbenzofuran	3-Benzylbenzofuran-2-aldehyde	"	"	"	117
C_{16}					
2,5-Diphenylfuran	2,5-Diphenylfuran-3-aldehyde	DMFA	$POCl_3$, 3 h, 100°	40	115
3-Benzyl-6-methoxybenzofuran	3-Benzyl-6-methoxybenzofuran-2-aldehyde	"	$POCl_3$, 8 h	good	117
C_{18}					
3-(3',4'-Dimethoxybenzyl)-6-methoxybenzofuran	3-(3',4'-Dimethoxybenzyl)-6-methoxybenzofuran-2-aldehyde	DMFA	$POCl_3$, 8 h	good	117

2. Sulphur- and selenium-containing heterocycles

C_4					
Thiophene	Thiophene-2-aldehyde	MFA	$POCl_3$, 20°-25°	75-77	122,141,142
Thiophene	Thiophene-2-aldehyde	DMFA	$POCl_3$, 1-2 h, 90°-95°	77	20,124,125
2-Chlorothiophene	5-Chlorothiophene-2-aldehyde	MFA or DMFA	$POCl_3$, 90°-95°	43-59	20,21,122
2-Bromothiophene	5-Bromothiophene-2-aldehyde	"	$POCl_3$, *o*-dichlorobenzene, 18 h, 20°	up to 70	21, 123
3-Bromothiophene	3-Bromothiophene-2-aldehyde	DMFA	$POCl_3$, boiling, 4.5 h	69	143
Selenophene	Selenophene-2-aldehyde	MFA	$POCl_3$, 65°	70	137
C_5					
2-Methylthiophene	5-Methylthiophene-2-aldehyde	MFA or DMFA	$POCl_3$, heat	66-81	20,122,124
3-Methylthiophene	3-Methylthiophene-2-aldehyde	"	$POCl_3$ or $SOCl_2$, heat	68-83	20,122,126
3-Methylselenophene	3-Methylselenophene-2-aldehyde	DMFA	$POCl_3$, 1 h, 50°-70°	72	138
C_6					
2-Ethylthiophene	5-Ethylthiophene-2-aldehyde	MFA	$POCl_3$, 100°	75-80	122
2,3-Dimethylthiophene	4,5-Dimethylthiophene-2-aldehyde	"	"	84.5	123
2,5-Dimethylthiophene	2,5-Dimethylthiophene-3-aldehyde	"	"	20	21,144
2-Acetamidothiophene	5-Acetamidothiophene-2-aldehyde	DMFA	$POCl_3$, 15 h, 95°	43	20,144,145
2,3-Dimethylselenophene	2,3-Dimethylselenophene-5-aldehyde	"	$POCl_3$, 65°	66	139
3,4-Dimethylselenophene	3,4-Dimethylselenophene-2-aldehyde	"	"	94	139
C_7					
2,3,5-Trimethylthiophene	2,3,5-Trimethylthiophene-4-aldehyde	MFA	$POCl_3$, 100°	38	123
2-Propylthiophene	5-Propylthiophene-2-aldehyde	"	"	77-85	122,127
2,3,4-Trimethylselenophene	2,3,4-Trimethylselenophene-5-aldehyde	DMFA	$POCl_3$, 65°	77	139
C_8					
2-n-Butylthiophene	5-n-Butylthiophene-2-aldehyde	MFA	$POCl_3$, 3 h, 25°-35°	80	128
2-t-Butylthiophene	5-t-Butylthiophene-2-aldehyde	"	"	76-99	20,21,128

TABLE 5. (contd.)

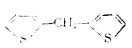
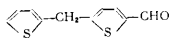
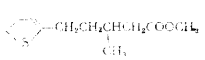
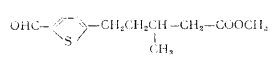
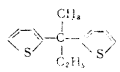
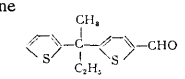
Starting material	Product	Formylating agent	Reaction conditions	Yield %	Reference
Thionaphthene	Thionaphthene-3-aldehyde	MFA	$POCl_3$, 16 h, 25°-35°	9	21, 135
4, 5, 6, 7-Tetrahydrothionaphthene	4, 5, 6, 7-Tetrahydrothionaphthene-2-aldehyde	"	$POCl_3$, heat	-	136
5-(β-acetoxyethyl)thiophene	5-(β-acetoxyethyl)thiophene-2-aldehyde	"	"	-	21, 130
C_9					
2-Methyl-5-t-butylthiophene	2-Methyl-5-t-butylthiophene-3-(or 4)-aldehyde	MFA	$POCl_3$, 3 h, 55°-65°	30.5	128
Bis(2-thienyl)methane 	1-(2'-Thenyl)thiophene-5-aldehyde 	"	$POCl_3$, 25°-35°	48	131
C_{10}					
2-Phenylthiophene	5-Phenylthiophene-2-aldehyde	MFA	$POCl_3$, toluene, 5 h	80	129
2-*m*-Chlorophenylthiophene	5-*m*-Chlorophenylthiophene-2-aldehyde	"	"	70	129
6-Ethoxythionaphthene	6-Ethoxythionaphthene-3-aldehyde	"	$POCl_3$, heating at 100°	-	36
2-(γ-Ethoxycarbonylpropyl)thiophene	5-(γ-Ethoxycarbonylpropyl)thiophene-2-aldehyde	"	$POCl_3$, 20°-25°	83	133, 134
2-(δ-Methoxycarbonylbutyl)thiophene	5-(δ-Methoxybutyl)thiophene-2-aldehyde	"	"	94	134
5-Methyl-2-(then-2-yl)thiophene	5-(5'-methyl-then-2'-yl)thiophene-2-aldehyde	"	$POCl_3$, 3 h, 55°-60°	44	128
C_{11}					
2-*m*-Tolylthiophene	5-*m*-Tolylthiophene-2-aldehyde	MFA	$POCl_3$, toluene, 5 h, 100°	77	129
2-(δ-Ethoxycarbonylbutyl)thiophene	5-(δ-Ethoxycarbonylbutyl)thiophene-2-aldehyde	"	$POCl_3$, 25°-35°	75-83	134
2-(γ-Methyl-δ-methoxycarbonylbutyl)thiophene 	5-(γ-Methyl-δ-methoxycarbonylbutyl)-thiophene-2-aldehyde 	"	"	84	134
C_{12}					
2, 5-Di-t-butylthiophene	2, 5-Di-t-butylthiophene-3-aldehyde	MFA	$POCl_3$, 3 h, 55°-60°	36	128
2, 2-Bis(2'-thienyl)butane 	2-(2'-Thienyl)-2-(5'-formylthien-2'-yl)butane 	"	$POCl_3$, 25°-35°	64	132
C_{16}					
2, 4-Diphenylthiophene	3, 5-Diphenylthiophene-2-aldehyde	MFA	$POCl_3$, toluene, 100°	-	129
2, 4-Diphenylselenophene	3, 5-Diphenylselenophene-2-aldehyde	"	$POCl_3$, toluene, 5 h, 100°	83.5	129
C_{18}					
2, 4-Di-*p*-tolylthiophene	3, 5-Di-*p*-tolylthiophene-2-aldehyde	MFA	$POCl_3$, 100°, toluene	82	129
2, 4-Di-*p*-tolylselenophene	3, 5-Di-*p*-tolylselenophene-2-aldehyde	"	"	83	129
2, 4-Di-*p*-anisylselenophene	3, 5-Di-*p*-anisylselenophene-2-aldehyde	"	"	69	129
3. Nitrogen-containing heterocycles					
C_4					
Pyrrole	Pyrrole-2-aldehyde	DMFA	$POCl_3$, dichloroethane, 30 min, 30°-40°	39-89	29, 34, 146
1-Methylpyrazole	1-Methylpyrazole-4-aldehyde	"	$POCl_3$, 1.5 h, 95°-100°	33	112
C_5					
Pyradine	Picolinic aldehyde	MFA	$POCl_3$, 100°	low	110
N-Methylpyrrole	*N*-Methylpyrrole-2-aldehyde	DMFA	$POCl_3$, dichloroethane, 30°-40°	79-90	34
C_8					
Indole	Indole-3-aldehyde	DMFA	$POCl_3$, DMFA, 30°-35°	95.5	29
"	"	MFA	$POCl_3$, dichloroethane, 100°	53.5	103
"	"	*N*-Formylindoline	$POCl_3$, trichloroethane, boiling, 30 min	25	26
Potassium indole	"	DMFA	$POCl_3$, 30°-35°, DMFA	72	104

TABLE 5. (contd.)

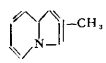
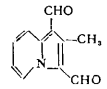
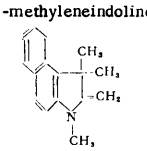
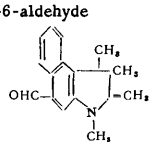
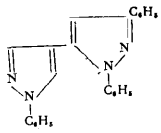
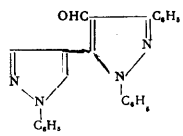
Starting material	Product	Formylating agent	Reaction conditions	Yield %	Reference
C_9					
2-Methylpyrrocoline 	1,3-Diformyl-2-methylpyrrocoline 	DMFA	$POCl_3$, 15 min, 50°-60°	28	107
2,4-Dimethyl-5-ethoxycarbonylpyrrole	2,4-Dimethyl-3-formyl-5-ethoxycarbonylpyrrole	DMFA	$POCl_3$, boiling, 2 h	96	106
1-Phenylpyrazole	1-Phenylpyrazole-4-aldehyde	"	$POCl_3$, DMFA, 4 h, 95°-100°	76	112
1-(*m*-Nitrophenyl)pyrazole	1-(*m*-Nitrophenyl)pyrazole-4-aldehyde	"	"	9	114
C_{10}					
N-Methyl-1,2,3,4-tetrahydroquinoline	*N*-Methyl-1,2,3,4-tetrahydroquinoline-6-aldehyde	MFA	$POCl_3$, benzene, 10-12 h, 20°	46	111
C_{11}					
2-Ethoxycarbonylindole	2-Ethoxycarbonylindole-3-aldehyde	MFA	$POCl_3$, dichloroethane, boiling, 1 h	99.5	103
5-Bromo-2-ethoxycarbonylindole	5-Bromo-2-ethoxycarbonylindole-3-aldehyde	DMFA	"	42	105
C_{12}					
1,2,3,4-Tetrahydrocarbazole	*N*-Formyl-1,2,3,4-tetrahydrocarbazole	DMFA	$POCl_3$, 8 h, 95°-100°	65	109
1,3,3-Trimethyl-2-methyleneindoline	1,3,3-Trimethyl-2-methyleneindoline-6-aldehyde	MFA	$POCl_3$, benzene, 5°-15°	80	142
C_{13}					
N-Methylcarbazole	*N*-Methylcarbazole-3-aldehyde	MFA	$POCl_3$, *o*-dichlorobenzene, 6 h, 100°	61	27
N-Methyl-1,2,3,4-tetrahydrocarbazole	-Methyl-1,2,3,4-tetrahydrocarbazole-*N*-7-aldehyde	DMFA	$POCl_3$, 8 h, 95°-100°	34	109
N-Methyl-6-nitrocarbazole	*N*-Methyl-6-nitrocarbazole-3-aldehyde	MFA	$POCl_3$, *o*-dichlorobenzene, 6 h, 100°	80	108
N-Methyl-6-bromocarbazole	*N*-Methyl-6-bromocarbazole-3-aldehyde	"	"	85	108
C_{14}					
N-Ethylcarbazole	*N*-Ethylcarbazole-3-aldehyde	MFA	$POCl_3$, 100°	-	36
2-Methyl-4-phenyl-5-ethoxycarbonylpyrrole	2-Methyl-4-phenyl-5-ethoxycarbonylpyrrole-3-aldehyde	DMFA	$POCl_3$, boiling, 2 h	97	106
C_{15}					
5-Benzyloxyindole	5-Benzyloxyindole-3-aldehyde	DMFA	$POCl_3$, 45 min, 35°	75	147
C_{16}					
N-Butylcarbazole	-Butylcarbazole-3-aldehyde	MFA	$POCl_3$, *o*-dichlorobenzene, boiling	81	108
4,5-Benzo-1,3,3-trimethyl-*N*-2-methyleneindoline 	4,5-Benzo-1,3,3-trimethyl-2-methyleneindoline-6-aldehyde 	"	$POCl_3$, benzene, 5°-15°	-	148
1,4-Diphenylpiperazine	1,4-Bis(4'-formylphenyl)piperazine	DMFA	$POCl_3$, 1.5 h, 95°-100°	-	81
N-Butyl-6-nitrocarbazole	*N*-Butyl-6-nitrocarbazole-3-aldehyde	MFA	$POCl_3$, *o*-dichlorobenzene, 6 h, 100°	85	108
N-Butyl-6-bromocarbazole	*N*-Butyl-6-bromocarbazole-3-aldehyde	"	"	90	108
C_{17}					
N-Isopentylcarbazole	-Isopentylcarbazole-3-aldehyde	MFA	$POCl_3$, *o*-dichlorobenzene, 6 h, 100°	85	108
N-Butyl-6-methylcarbazole	*N*-Butyl-6-methylcarbazole-3-aldehyde	"	"	85	108
-Isopentyl-6-nitrocarbazole	*N*-Isopentyl-6-nitrocarbazole-3-aldehyde	"	"	85	108
C_{19}					
N-Benzyl-1,2,3,4-tetrahydrocarbazole	*N*-Benzyl-1,2,3,4-tetrahydrocarbazole-*N*-7-aldehyde	DMFA	$POCl_3$, 8 h, 95°	36	109

TABLE 5.(contd.)

Starting Material	Product	Formylating agent	Reaction conditions	Yield %	Reference
C_{24} 1,3,1'-Triphenyl-5,4'-bipyrazole 	1,3,1'-Triphenyl-5,4'-bipyrazole-4--aldehyde 	DMFA	$POCl_3$, DMFA, 4 h, 95°-100°	83	114

4. Heterocycles with more than one hetero-atom

C_{10} 4-Phenylmorpholine	*p*-(4-Morpholinyl)benzaldehyde	DMFA	$POCl_3$, 1-2 h, 95°-100°	2	81
C_{13} 10-Methylphenothiazine	10-Methylphenothiazine-3-aldehyde	MFA	$POCl_3$, 4 h, 100°	88	140
C_{14} 10-Ethylphenothiazine	10-Ethylphenothiazine-3-aldehyde	MFA	$POCl_3$, 4 h, 100°	82.5	140
3,10-Dimethylphenothiazine	3,10-Dimethylphenothiazine-7-aldehyde	"	"	42	140
C_{15} 3-Methyl-10-ethylpheno-thiazine	3-Methyl-10-ethylphenothiazine-7--aldehyde	MFA	$POCl_3$, 4 h, 100°	72	140
10-Phenylphenothiazine	10-Phenylphenothiazine-3-aldehyde	"	"	63	108

* Dimethylformamide.

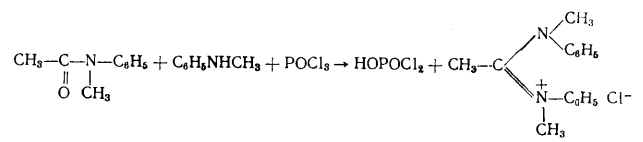
** Methylformanilide.

III. ACYLATION OF ORGANIC COMPOUNDS

Although discovered before formylation, other acylations of the various types of organic compounds with substituted carboxylic amides has been studied much less thoroughly than their formylation.

In 1896 Friedel[149] studied the reaction between *N*-methylacetanilide and $POCl_3$, which ensued upon heating the reactants at 120°. He continued the heating as long as HCl was evolved, and then, by treating the melt with soda solution, he obtained a dye, to which, upon analysis, he ascribed the formula $C_{22}H_{20}N_2Cl_2$. The structure of that dye remained unknown until Fischer and his colleagues[10] established that in the Friedel reaction, under the action of $POCl_3$, the acetyl group of one molecule of methylacetanilide was split off and attached to the nucleus of another such molecule, in the *o*-position with respect to the *N*-acetylamino group. The *o*-acetamidoacetophenone, which was thereby formed, was subsequently transformed into a cyanine dye.

Methylaniline formed in this reaction condenses easily in the presence of $POCl_3$ with unreacted methylacetanilide yielding *N*,*N*'-diphenyl-*N*,*N*'-dimethylacetamidinium chloride. This accords with the usual scheme for the formation of amidines from arylamides and secondary aliphatic--aromatic amines under the action of phosphorus halides[150]:



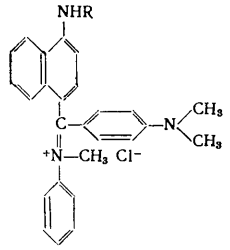
The amidine formed is presumed[11] to be even more capable of acylating the aromatic ring than the initial methylacetanilide.

Fischer's work proved the migration of the acetyl group from one molecule of aryl-*N*-alkylacetamide into the aromatic ring of another, and provided an explanation for the mechanism of a series of similar transformations, described in the patent literature[151-156].

By heating benzanilide with dimethylaniline and $POCl_3$ at 120°, 4-dimethylaminobenzophenone anil is formed[150]. Diethylaniline behaves similarly in this reaction.

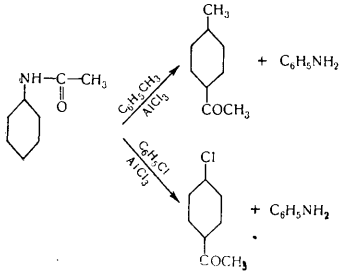
Noelting[152,153] patented the reaction for the introduction of the *p*-dimethylaminobenzyl group into the nucleus of *N*-methyl-α-naphthylamine, *N*-ethyl-α-naphthylamine, and *N*-phenyl-α-naphthylamine, by means of *N*-methyl-*p*-di-

methylaminobenzanilide in dimethylaniline solution. Here the reaction products are dyes similar in their properties to auramine:

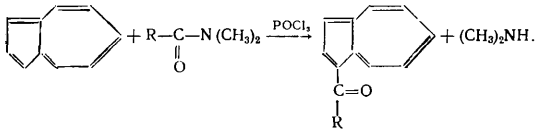


where R = CH_3, C_2H_5, C_6H_5.

The uses of benzoyl-*m*-xylidine[148], *N*-methylbenzanilide[154,155], *m*-methoxybenzanilide[155], and α-naphthanilide[156] as acylating agents have been reported in patents. Acetanilide in the presence of $AlCl_3$ is also capable of acylating the benzene ring in toluene and chlorobenzene[157,158].



This reaction proceeds via the intermediate formation of acetyl chloride, followed by a Friedel-Crafts ketone synthesis, i.e. as in the case of the molecular rearrangement of anilides[159]. The more reactive aromatic hydrocarbons react with substituted amides even under ordinary conditions. Hafner and Bernhard[160] developed a very elegant method for the preparation of azulenic ketones by acylation of azulene with different *N*,*N*-dimethylcarboxamides. The reaction is carried out in the presence of $POCl_3$, by boiling for 4 h in tetrahydrofuran solution.



1-Acetylazulene, 1-benzoylazulene, 1-lauroylazulene, and ω-ethoxycarbonylhexyl(1-azulyl)ketone were prepared by this method.

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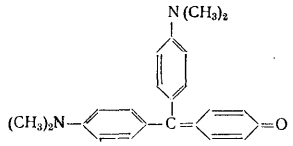
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INFLUENCE OF THE SOLVENT ON THE COLOUR OF DYES (SOLVATOCHROMISM)

A. I. Kiprianov

The colour of organic dyes always depends to a certain extent on the solvent. Acid and alkaline solvents change the colour of dyes by forming salts with them, but in most cases neutral solvents have little influence on the absorption of light by the dyestuff. There exists, however, a certain number of dyestuffs (or coloured substances) which change colour very markedly on passing from one completely neutral solvent to another. This has received the name "solvatochromism".

A classic example of solvatochromism is that exhibited by tetramethyldiaminofuchsone (I), prepared by Schlenk in 1909[1]:



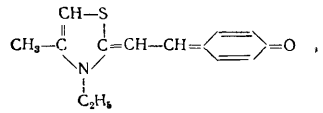
(I)

This dyestuff is yellow in benzene solution and red-violet in alcohol. Schlenk considered the change of colour as due to a change of molecular weight; the fuchsone giving a true solution in alcohol, but polymers being formed in benzene and the dyestuff dissolving as a colloid. This explanation of the solvatochromic effect in tetramethyldiaminofuchsone, as in other dyes, has since been shown to be false[2]; they dissolve, in organic solvents at least, to form monomolecular solutions.

Up to the 1940's, the solvatochromic effect was explained on the basis of the old views of the dyestuff molecule as one containing a stable system of valency bonds. Of various theories of this type by various workers[2,3,4], we shall consider only one – that of the formation of characteristically coloured complexes of the molecules with solvent molecules[2], since this type of theory is met even in later publications[5,6].

The attempt to explain solvatochromism in dyes by the formation of simple complexes with the solvent must be discarded mainly on the evidence of the study of the absorption spectra of such dyes in mixed solvents.

Kiprianov and Timoshenko[7] obtained the absorption curves of the dyestuff (II):



(II)

which shows a clear solvatochromic effect. These curves are shown in Fig. 1 (*A* in pyridine, *B* in water, and *C* in a

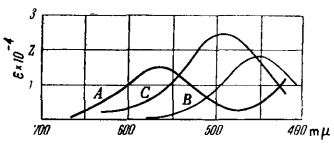


Fig. 1.

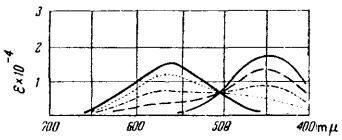
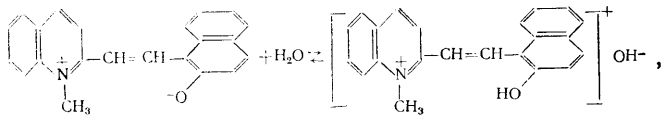


Fig. 2.

1 : 1 mixture of pyridine and water). The absorption maximum of (II) in pyridine lies at 580 mμ, and in water at 455 mμ. If the dyestuff were present in pyridine and in water as two different complexes, in the pyridine–water mixture two maxima would be observed, at the same wave-lengths as for the solution of (II) in pyridine and in water. In pyridine–water mixtures of varying composition, these curves would have a common point of intersection (the isobestic point), as shown in Fig. 2.

In actual fact, the primary maxima do not appear on the absorption curve of (II) in the 1 : 1 pyridine–water mixture (Fig. 1, *C*), but a new maximum is found at 495 mμ. Thus in the mixed solvent, (II) behaves not as an equimolar mixture of two different complexes, but as an individual substance of a new structure.

In 1940 Wizinger and Wenning[5] synthesised the dyestuff (III), which changed colour on adding water to its pyridine solution. This solvatochromic effect was explained as due to the reversible addition of a molecule of water, with the formation of the ionised hydroxide (IV):

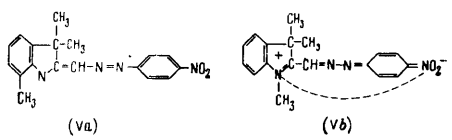


(III) (IV)

Brooker[8] showed that this explanation is incorrect. The absorption curve of the aqueous pyridine solution shows that it contains an individual substance, and not a mixture of the two compounds, the hydrated and the non-hydrated. The absorption spectrum of the cation of the hydroxide (IV) should be the same as that of the cation of the corresponding iodide, but in fact they are different.

It might be suggested that when they are formed, the complexes with solvent molecules of the dyestuffs showing the solvatochromic effect are solvates consisting of a large number of oriented solvent molecules; as the composition of the solvent changes gradually, the solvates are gradually converted into solvates of different composition. This raises the question why the formation of solvates should influence the colour of solutions of certain dyestuffs only, and not of them all. This is the more surprising since basic and acid dyes, which dissociate in solution into ions, do not exhibit the solvatochromic effect, although their ions are, of course, strongly solvated. It must be assumed that the reason for the solvatochromic effect lies not only in solvation, but also in the structural features of the molecules of those dyes for which the solvatochromic effect is observed. The structure of these dyes must be capable of gradual changes under the influence of changes in the medium, these changes providing an infinite number of intermediate forms.

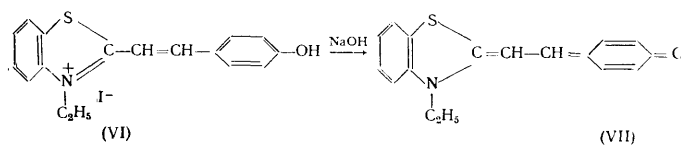
König came very close to such a viewpoint in 1924.[9] He observed a solvatochromic effect in a number of "endohalochromic" (in his terminology) azo-dyes of the type of (V):



(V*a*) (V*b*)

According to König, the structure (V*a*) is "at least equivalent" to the structure (V*b*), and between these two extreme states of the molecule, a number of intermediate states, which cannot be expressed in valency formulae, are possible.

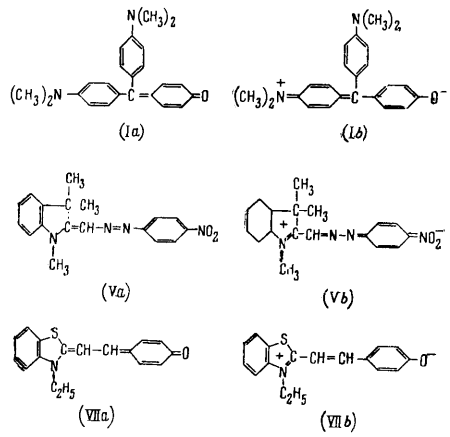
In 1940 Kiprianov and Petrun'kin[10,11] and later Kiprianov and Timoshenko[7,12,13] synthesised a series of yellow dyestuffs, the hydroxystyryl compounds of type (VI), and found that when they react with alkali, the anhydro bases (VII) are formed, these showing a clear solvatochromic effect:



(VI) (VII)

This effect is the opposite of that with tetramethyldiaminofuchsone. Whereas the absorption of the fuchsone shifts to shorter wave-lengths on passing from non-polar to polar solvents, the anhydro bases of the type (VII) react in the opposite sense to the polarity of the solvent.

The explanation of solvatochromism proposed in 1940 by Kiprianov and Petrun'kin is as follows. Attention was drawn to the fact that the solvatochromic effect is shown by dyestuffs of the so-called merocyanine * structure, that is to say, those for which two formulae may be written, one non-polar (*a*) and the other dipolar (*b*), for example:



(I*a*) (I*b*)

(V*a*) (V*b*)

(VII*a*) (VII*b*)

The actual molecular structure of each dyestuff which exhibits the solvatochromic effect is intermediate between the two formulae, and is determined by the polarising influence of the medium, the shortest absorption wave-length corresponding to that constitution of the merocyanine dyestuff at which the electrons in the conjugated chain are most evenly spread. It now becomes clear why two types of solvatochromism are observed: those merocyanine dyestuffs whose structure in the given solvent is nearer the non-polar form will absorb at a shorter wave-length on passing to a more polar solvent, since in polar solvents their molecule approaches the condition in which the electron density is most evenly distributed; those dyestuffs which have a structure approaching the dipolar form will, on the other hand, absorb at a shorter wave-length on passing to a less polar solvent.

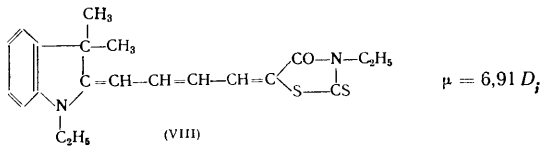
* In the original Russian the term intra-ionoid was used here and elsewhere in the review. It has been rendered as mexocyanine throughout (Ed. of Translation).

Kiprianov and Petrun'kin named the shift of absorption to shorter wave-lengths when the polarity of the solvent is decreased [as for the anhydro bases (VII)] the solvatochromism of the first type, and that when the polarity of the solvent is increased [as for the fuchsone (I)] solvatochromism of the second type. Brooker[14] later named the fuchsone type of effect normal solvatochromism, and the opposite effect reverse solvatochromism. Dimroth[15] uses the terms positive and negative solvatochromism respectively. We shall use Dimroth's terminology.

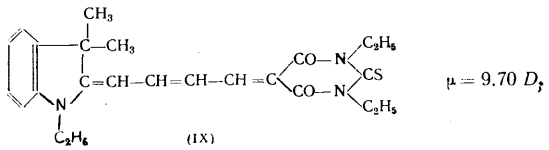
This elementary theory gives a good explanation of a number of other properties of merocyanine dyestuffs. It is known that they are adsorbed on polar adsorbents, changing their colour according to the type of solvatochromic effect they exhibit[16]. Merocyanine dyestuffs change their colour on heating the solution (thermochromism), the change again depending on the type of solvatochromic effect: with a positive effect the absorption wave-length is reduced, and with a negative effect it is increased on heating. This is due to the change in the polarising action of the solvent on increasing the temperature (loss of orientation of the solvating molecules).

The solvatochromic effect in merocyanines is observed in their fluorescence spectra as well as their absorption spectra; the change in the fluorescence spectra under the influence of the solvent has been studied mainly on simple merocyanine analogues, such as phthalimide and maleimide derivatives[17]. The relationship between the fluorescence spectra and the polarising power of the solvent is the same as for the absorption spectra.

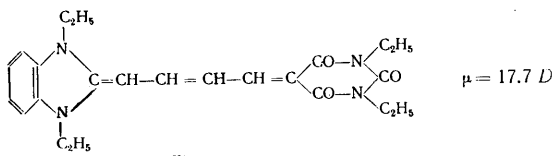
A direct confirmation of the above theories on the nature of the solvatochromic effect is given by Kushner and Smyth's determination in 1949 of the dipole moments of the merocyanine dyestuffs (VIII)–(X)[18]:



(VIII) $\mu = 6{,}91\ D$;



(IX) $\mu = 9.70\ D$;



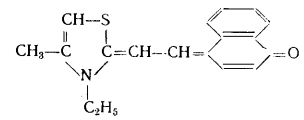
(X) $\mu = 17.7\ D$.

The calculations show that if the dyestuffs existed only in the non-polar form, their dipole moments would not exceed 2 *D*. In fact, the dipole moment of (X) (17.7 *D*) almost corresponds to that of the dipolar ion, while from its dipole moment (IX) (9.70 *D*) may be considered to be approximately half polarised. The merocyanine (VIII) shows a positive solvatochromic effect, the merocyanine (IX) suffers almost no change of colour on passing from polar to non-polar solvents, while (X) possesses a negative solvatochromic effect. The dipole moments of a number of other merocyanine dyestuffs have been determined, in relation to their solvatochromic effects, by Syrkin, Levkoev, and coworkers[19].

The above views on the nature of the solvatochromic effect in dyestuffs are now generally accepted. Almost at the same time as Kiprianov, they were proposed (without experimental confirmation) by Förster[20], and were later developed by Brooker and coworkers[8,21], Knott[22], Dimroth[15,23,24], and recently by Hünig[25,26].

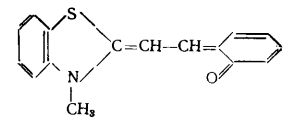
Hünig introduces the concept of the degree of solvatochromism, i.e. the amount by which the absorption maximum of various merocyanine dyestuffs is displaced on passing from one solvent to another, for example from methanol to chloroform. Brooker and coworkers[14] showed that the degree of solvatochromism of merocyanines increases as the polymethine chain increases in length.

As well as dyestuffs showing positive or negative solvatochromism, dyestuffs of intermediate type must exist, i.e. those in which maximum spreading of electron density (equalisation of the bonds) is achieved in a solvent of medium polarity; in such a case, passing from this solvent to a more polar or a less polar one would be accompanied by a decrease in the absorption wave-length. Such dyestuffs were found among the merocyanines by Levkoev, Sveshnikov, and Lifshits[27], and then among hydroxystyryl anhydro-bases by Kiprianov and Timoshenko[13]. An example of a dye with "intermediate" solvatochromism is (XI),



(XI)

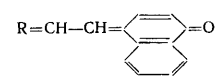
with absorption maxima at 506 mμ in water, 594 mμ in alcohol, 592 mμ in chloroform, and 574 mμ in benzene. Kiprianov and Timoshenko showed[7,13] that by making gradual alterations in the structure of the nuclei of hydroxystyryl anhydro-bases, it is possible to pass from negative solvatochromism through a compound of intermediate type to positive solvatochromism. For example, if in compound (XII)



(XII)

the *o*-benzoquinone nucleus is successively replaced by *p*-benzoquinone, 1,2-naphthoquinone, and 1,4-naphthoquinone, the relationship between the corresponding anhydro-bases and the polarity of the solvent changes in the same order as the reduction potentials of the quinones. The *o*- and *p*-benzoquinone derivatives show negative solvatochromism, the 1, 2-naphthoquinone derivative solvatochromism of intermediate type, and the 1,4-naphthoquinone derivative positive solvatochromism.

If the solvatochromism of the anhydro-bases of the general formula (XIII)

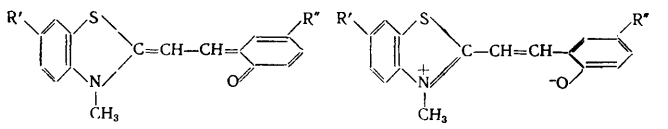


(XIII)

is compared, the molecules containing the same 1,4-naphthoquinone residue but different nitrogen-containing heterocycles R, it is found that with a very basic heterocycle (pyridine), the solvatochromism is negative, with hetero-

cycles of medium basicity (quinoline, thiazole) it is of intermediate type, and with weakly basic heterocycles (benzothiazole, indolenine), it is positive.

Finally, the nature of the solvatochromism can be altered by introducing polar substituents into the molecule of the merocyanine dyestuff[7,12,15,28,29]. If the benzothiazole nucleus of (XII) is substituted by R' or the quinone nucleus by R", we obtain dyes of structure (XIV).

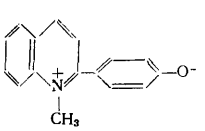


(XIV*a*) (XIV*b*)

Electropositive substituents in the benzothiazole nucleus [R' = OC_2H_5, $N(CH_3)_2$] cause the structure of the dye to approximate to the form corresponding to (XIV*b*), i.e. the form to which it is close even without the substituent; a decrease in the absorption wave-length is therefore observed in all solvents. The same substituents in the quinone nucleus [R" = OC_2H_5, $N(CH_3)_2$] cause the structure to approximate to the form (XIV*a*), and greatly deepen the colour. Electronegative substituents (e.g. NO_2) cause the opposite effects. By introducing an electronegative substituent R' and an electropositive substituent R", the negative solvatochromism of (XII) may be converted into positive.

In 1950 Kiprianov and Timoshenko[7] determined the absorption curves of several merocyanine dyes in a water–pyridine mixture. An interesting effect was observed: the intensity of absorption was greater in aqueous pyridine than in water or pure pyridine (Fig. 1). Brooker and coworkers, studying solvatochromism in mixed solvents in more detail[8], showed that the increase in the intensity of absorption, like the shift to shorter wave-lengths, is associated with the dyestuff molecule approaching the condition exactly intermediate between the non-polar and the dipolar forms; Brooker named this condition the isoenergetic point. It is particularly easily determined from the intensity maximum of the dye in mixtures of two solvents. For example, for (VII) in mixtures of pyridine with water, the isoenergetic point lies at 92.5 vol. % of pyridine (Fig. 3).

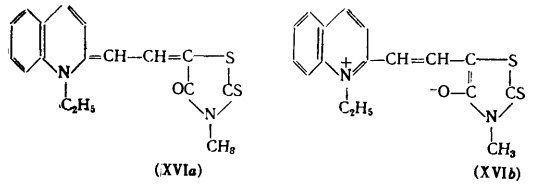
We shall now consider several typical examples of solvatochromism in dyes of various classes. After Kiprianov and Petrun'kin's work[10,11], the hydroxystyryl anhydro-bases became the most frequently studied in investigations of solvatochromism[8,12,14,22–26,30]. It is interesting that the solvatochromism of hydroxystyryl anhydro-bases had been observed in 1930 in König's laboratory[31]. No explanation of this effect was found, and the work was not published. The anhydro-bases of 2-hydroxyphenyl derivatives of heterocyclic nitrogen compounds, of type (XV),



(XV)

are similar in structure to those of hydroxystyryl compounds, and also exhibit solvatochromism[24,30].

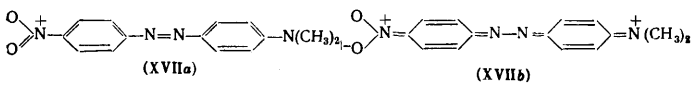
Brooker[14] and Levkoev[27,32] and their coworkers studied the solvatochromism of merocyanines, of type (XVI), in great detail.



(XVI*a*) (XVI*b*)

In most cases the merocyanines show positive solvatochromism, i.e. their structure is nearer the (*a*) form; however, if one nucleus is very positive and the other very negative, the solvatochromism may be negative (X).

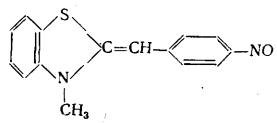
Azo-compounds change colour in solvents of differing polarity if one aromatic ring carries an electropositive substituent and the other an electronegative one. An example is the aminoazo-dye (XVII).



(XVII*a*) (XVII*b*)

The solvatochromism of these dyes is very positive, since in any solvent the structure is nearer (XVII*a*) than (XVII*b*), which contains two quinonoid nuclei.

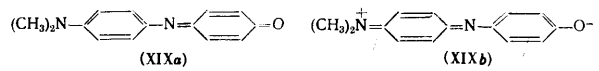
Positive solvatochromism is also found in nitroso-dyes of type (XVIII).



(XVIII)

However, if the benzothiazole nucleus carries a nitro group, the solvatochromism is negative[7]. The azo-dyes obtained from quaternary salts of heterocyclic nitrogen compounds, e.g. (V), which have been studied by König[9,31] and Kiprianov and Timoshenko[7], behave similarly.

Phenol blue (XIX) is of the tetramethyldiaminofuchsone (I) type[21,33,34].



(XIX*a*) (XIX*b*)

The positive solvatochromism of this dye, like that of tetramethyldiaminofuchsone, is due to the dipolar structure (XIX*b*) being less favourable, because of the separation of the ionic charges.

A somewhat more complex system is that of the pyrazolone-azomethines (XX), whose solvatochromism was studied by Vittum and coworkers[29]. In discussing the interaction of (XX) with solvents, at least three structures,

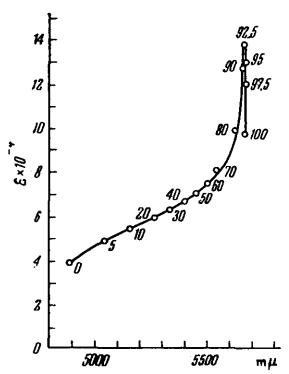
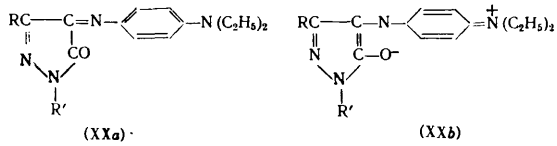
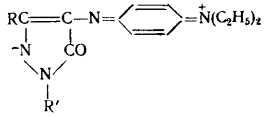


Fig. 3.

one non-polar and two dipolar, must be taken into account:



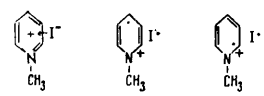
(XXa) (XXb)



(XXc)

We have thus far considered only those merocyanine dyes in which there is conjugation between the atoms carrying the positive and negative charges. The structure of such a dye can always be represented in a non-polar form. It is interesting, however, that solvatochromism is also observed with coloured dipolar compounds in which there is no conjugation between the positive and negative centres, and which consequently exist only in the betaine form. The solvatochromism of these betaines has recently been discussed by Kosower[35,36].

We may consider *N*-alkyl pyridinium salts as models of betaines in which there is no conjugation between the ionic centres. The absorption band of pyridine methioxide is displaced towards longer wave-lengths as the polarity of the solvent is decreased; this salt shows negative solvatochromism. It is assumed that in the ground state pyridine methiodide exists as the ion pair (XXI*a*). Under the action of a quantum of light, the electron of the iodide ion is transferred to the pyridine nucleus, giving (XXI*b*), or, what is equivalent, (XXI*c*):



(XXIa) (XXIb) (XXIc)

Formulae (XXI*a*) and (XXI*b*) may be represented schematically as in Figs. 4 and 5.

Thus according to Kosower, at the moment of excitation by the light quantum, the dipole moment of the molecule becomes perpendicular to the original. However, the solvent-molecule dipoles which are oriented with respect to the dipole of the unexcited molecule do not have time to rotate, in accordance with the Frank-Condon principle. The energy required to rotate the dipole of the molecule in various solvents affects the magnitude of the quantum of absorbed light.

According to Kosower and Ramsey[36], the same is true for betaines of type (XXII*a*), which are yellow in water and blue-purple in heptane; here also one electron passes from the cyclopentadiene ring to the pyridine nucleus (XXII*b*). However, for betaines of type (XXII*a*), as for all the betaines described later, the excited state may be represented not as a diradical (XXII*b*), as was done by Kosower, but as another dipolar form (XXII*c*), formed from (XXII*a*) as a result of the transfer of an electron pair from the cyclopentadiene nucleus to the pyridine nucleus.

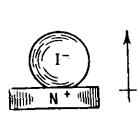


Fig. 4.

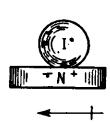
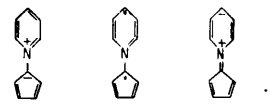


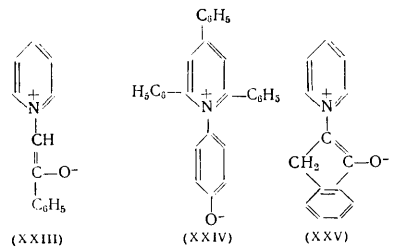
Fig. 5.



(XXIIa) (XXIIb) (XXIIc)

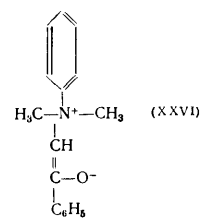
The possibility then arises of considering these betaines from the same point of view as the merocyanine dyes described above, bearing in mind that (XXII*a*) must be more polar than (XXII*c*).

Solvatochromism is observed in the pyridinium betaines described by Krönke (XXIII)[37], Dimroth (XXIV)[15,24,38], and Stafford (XXV)[39]:



(XXIII) (XXIV) (XXV)

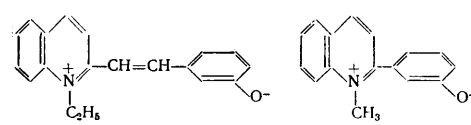
All these compounds show negative solvatochromism; they have low stability in solutions, and are easily oxidised and decolorised. The colourless compound (XXVI)



(XXVI)

apparently does not exhibit solvatochromism[39]; the transfer of electrons from the oxygen to the benzene ring is hindered by the absence of conjugation.

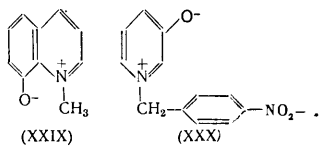
Solvatochromism and thermochromism are shown by the anhydro-bases of the *m*-hydroxystyryl compounds (XXVII)[24] and their lower vinylogues (XXVIII)[30], in which there is no conjugation between the charged atoms:



(XXVII) (XXVIII)

These betaines differ from their *o*- and *p*-isomers by their low stability and poor solubility in non-polar solvents. This type of betaine includes the anhydro-bases in which the ionic centres are in a single condensed system (XXIX)

or even in a single nucleus (XXX)[30] but are not in conjugation:



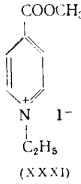
(XXIX) (XXX)

The betaine (XXIX) gives a red solution in water and a violet one in benzene; (XXX) absorbs at a shorter wave-length in chloroform than in alcohol. Apparently these betaines, for which a non-polar structure is impossible, exhibit only negative solvatochromism.

We shall now consider the part played by the dielectric constant of the solvent in solvatochromism. Solvatochromism clearly depends on the polarity of the solvent, but in earlier studies of solvatochromism[11] it was stated that no complete parallel was observed between the change of colour of a merocyanine dye and the change in dielectric constant of the solvent. Solutions of certain dyes had the same colour in chloroform and nitrobenzene, although the dielectric constants are 5.1 for chloroform and 36 for nitrobenzene; often the colour in methanol (ϵ = 32.6) is the same as in formamide (ϵ = 109.5)[25,33,40].

Kosower[35] discusses the significance of the dielectric constant in solvatochromism in detail. The dielectric constant, as is known from solvolysis studies[41], cannot be considered as a quantitative measure of the polarising power of the solvent; it reflects the behaviour of the solvent molecules in an electric field, but it does not take into account the form of the solvent molecule, the polarity of the individual bonds between the atoms, or other factors which are of great significance in the interaction with the solute. According to Kosower, a single compound for which the absorption of light changes greatly over a wide range of solvents must be chosen as standard; the displacement of the absorption maxima of this standard in these solvents will then give a scale for the polarity of the solvents.

Kosower proposes to use 1-ethyl-4-methoxycarbonylpyridinium iodide (XXXI) as standard:



(XXXI)

It is very soluble in water and in organic solvents, and the position of the absorption maximum is extremely sensitive to change in the polarising power of the solvent. As a measure of the ionising capacity of the solvent, Kosower uses Z, the energy of transfer of an electron in kcal mole^{-1}, calculated for the absorption maximum of the solution of (XXXI) in the given solvent. The calculation is made from the formula

$$Z = h\nu = 2.859 \times 10^{-3}\ \tilde{\nu}\ \text{cm}^{-1} = \frac{2859}{\lambda_{m\mu}}\ .$$

The values of Z were measured for various solvents and mixtures of solvents from chloroform (Z = 63.2) to 70% alcohol (Z = 86.4). For paraffinic hydrocarbons, in which

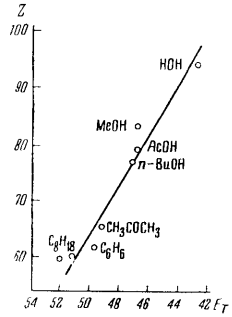


Fig. 6.

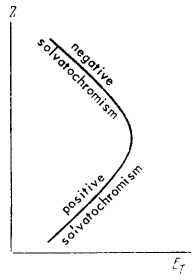


Fig. 7.

(XXXI) is insoluble, the standard used was pyridine N-oxide, which is soluble in hydrocarbons and also exhibits solvatochromism.

If Z is plotted against the energy of electron transitions ($E_T = h\nu$) at the absorption maxima of the merocyanine compound in each solvent, the points lie, according to Kosower, on a single straight line. Fig. 6 is such a curve constructed for phenol blue (XIX).

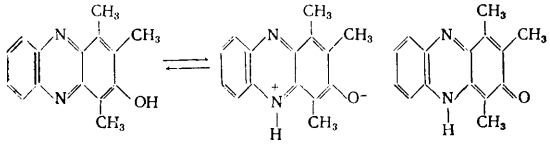
According to Kosower, this graph can be used to forecast the absorption maximum for phenol blue in any new solvent (except chloroform and pyridine) to within ± 8 mμ.

The determination of the ionising power of a solvent by using a standard solute is very useful, but Kosower is incorrect in considering that the points on the plot of Z against E_T for each merocyanine compound must lie on a straight line. In fact many such dyes, as we saw above, reach an isoenergetic point at a definite solvent ionising power, when the frequency and intensity of absorption of the solution is greatest; further increase of the ionising power of the medium changes the solvatochromism from positive to negative. For such substances, the plot of Z against E_T must be a curved line, of the general form shown in Fig. 7. Furthermore, as noted by Kosower himself, complex dyestuff molecules may exhibit large deviations from the general relationship owing to their specific interactions with the solvent molecules, depending on their size and shape.

Kosower remarks[35] that Z varies within much wider limits in hydroxylated solvents (from 71.3 in t-butanol to 94.6 in water) than in non-hydroxylated solvents (from 60.1 in isooctane to 71.3 in acetonitrile). This indicates the large part played by hydrogen bonds in solvatochromism.

The significance of hydrogen bonds in solvatochromism has been remarked upon several times. In their study of the absorption spectra of certain merocyanines, Bayliss and McRae[40] point out that they depend more on the ability of the solvent to form hydrogen bonds than on its dielectric constant. Kumler[42] makes the same comment in respect of *p*-nitroaniline. However, most workers[25,35,42] agree that hydrogen bonds play a substantial, but not the main, part in solvatochromism.

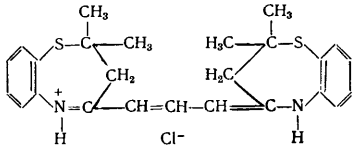
In 1947 John[43] described the solvatochromism of trimethylhydroxyphenazine (XXXII):



(XXXII) (XXXIIa) (XXXIIb)

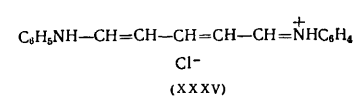
He correctly ascribed the change of colour of this compound to two factors, the tautomeric conversion of the hydroxy--form (XXXII) to the oxo-form (XXXIII*a*) or (XXXIII*b*). The hydroxy-form is yellow, while the oxo-form changes colour from red to violet, depending on the solvent. The difference in the colours is here so great that John proposed the use of this reagent for the analysis by absorption spectra of mixtures of various solvents. Later, the solvatochromism of trimethylhydroxyphenazine was studied by two other workers[44], who concluded that the change of colour is due exclusively to the formation of hydrogen bonds with the solvent, but the proofs which they give (for instance, the disappearance of solvatochromism on methylation of the hydroxy group) are not very convincing.

However, there apparently do exist cases where the main cause of the change of colour of a compound is the formation of hydrogen bonds with the solvent. Recently Mushkalo[45] described the solvatochromism of some new cyanine dyes which he prepared, containing hydrogen atoms in place of the hydrocarbon radicals on the ring nitrogen atoms, such as the dye (XXXIV):



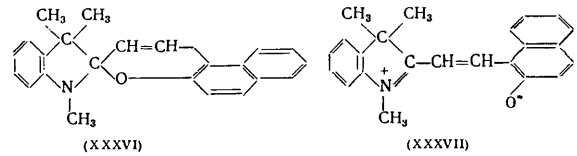
(XXXIV)

This dye, which does not have a merocyanine structure, gave absorption maxima at 550 mμ in chloroform and at 500 mμ in all oxygen-containing solvents (alcohol, acetone, formamide). The addition to a solution of (XXXIV) of small quantities of alcohol or acetone produced a sharp displacement of the absorption band towards shorter wave--lengths. Mushkalo reported analogous effects in other dyes containing the NH group as part of a ring or in side chains. However, the absorption maxima of salts of the dianils of glutaconic aldehyde, e.g. (XXXV), are the same in chloroform and alcohol.



(XXXV)

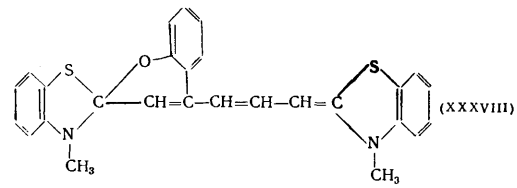
Solvatochromism and thermochromism may be associated with the opening and closing of spiro-rings. In 1940 Wizinger and Wenning[5] showed that colourless spiro-compounds of type (XXXVI)



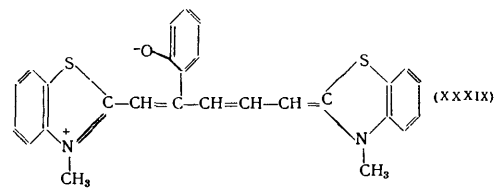
(XXXVI) (XXXVII)

are converted into (XXXVII) on heating or on solution in highly polar solvents, becoming intensely coloured. Knott[22] discusses the thermochromism and solvatochromism of spiro-compounds of type (XXXVI) in detail.

A case where the closing of the spiro-ring leads not to decolorisation but merely to a change in colour is that of the dicarbocyanine (XXXIX)[46], which in benzene gave a bright yellow solution, corresponding to the spiro-form (XXXVIII), but in alcohol is completely converted into the dark-blue form (XXXIX):



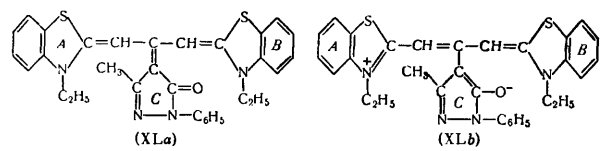
(XXXVIII)



(XXXIX)

The spectra of solutions in acetone and chloroform indicated the simultaneous presence of the yellow and blue tautomers.

The last type of solvatochromism to which we shall refer is associated with the spatial configuration of the dyestuff molecule. If there is conjugation between aromatic or heterocyclic nuclei in a dyestuff molecule, these nuclei are coplanar. If one of the nuclei leaves the plane in which the others lie and becomes perpendicular to it, this nucleus no longer takes part in the conjugation and ceases to influence the colour of the dyestuff. Brooker synthesised the trinuclear dye (XL):



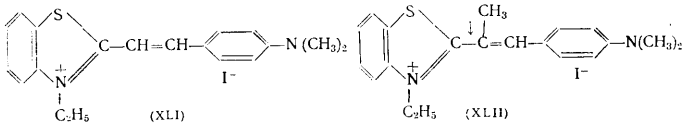
(XL*a*) (XL*b*)

A three-dimensional model of this compound shows that all three rings cannot be simultaneously coplanar. Assuming that rings *A* and *B* are coplanar and ring *C* is rotated through 90°, then ring *C* does not take part in the conjugation, and we have a typical carbocyanine with an absorption maximum at 550 mμ. This is the form in which (XL) exists in highly polar solvents (water, alcohol). On the other hand, in solvents of low polarity (lutidine), ring *A* (or *B*) leaves the plane of the other rings, and the absorption band is displaced towards shorter wave-lengths, since when rings *A* and *C* (or *B* and *C*) are coplanar, we have a typical

merocyanine with its characteristic absorption band. This type of stereosiomerism, associated with the polarising power of the solvent, was first described by Brooker[47,48], and named by him allopolar isomerism.

Allopolar isomerism is an example of how steric hindrance can change the structure and colour of a dye in solution. The influence of steric hindrance in the molecule on the absorption of light is much discussed in the literature, but no one has yet studied the influence of steric hindrance on the solvatochromism of simple merocyanine dyes. Kiprianov and Mikhailenko[49] have recently obtained some results on this question.

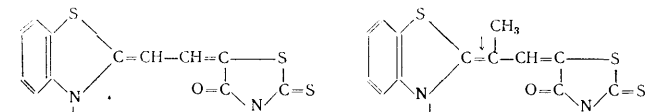
At present we know[50,51,52] that the partial destruction of the coplanarity of the rings in dyestuff molecules always leads to a reduction in the intensity of absorption, and almost always to a displacement of the absorption maximum; if a ring rotates about a single (or predominantly single) bond, the absorption maximum is displaced towards shorter wave-lengths. This is observed, for example, in the styryl dyes (XLI) and (XLII).



(XLI) (XLII)

in alcohol λ_{max} 530 mμ λ_{max} 481 mμ

Strains caused by the methyl group induce the benzothiazole ring in (XLII) to rotate by a certain angle about the single bond marked by the arrow, as a result of which the absorption band is displaced towards shorter wave-lengths. Similar steric hindrance in the merocyanine molecule (XLIV)

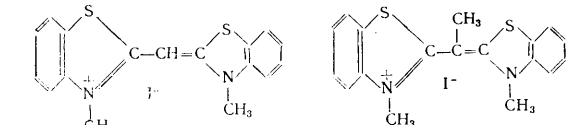


(XLIII) (XLIV)

in alcohol λ_{max} 524 mμ λ_{max} 541 mμ

causes rotation about the double bond, and the absorption maximum is displaced towards longer wave-lengths.

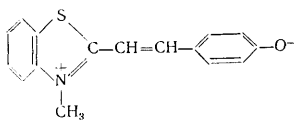
In the symmetrical monomethine cyanine (XLV), in which both bonds joining the thiazole rings are equivalent and of the order ~ 1.5, destruction of the coplanarity of the rings also causes a shift of absorption to shorter wave-lengths [longer wave-lengths ? (Ed. of Translation)].



(XLV) (XLVI)

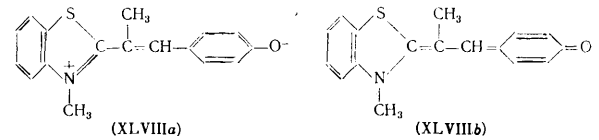
in alcohol λ_{max} 422 mμ λ_{max} 465 mμ

Knowing the above effects, it is possible to forecast to a considerable extent how the destruction of the coplanarity of the rings in simple merocyanine dyes will affect their absorption of light. If a methyl group is introduced at the β-position of the chain in the hydroxystyryl anhydro-base (XLVII)



(XLVII)

the dye (XLVIII), with a non-planar molecule, is formed,



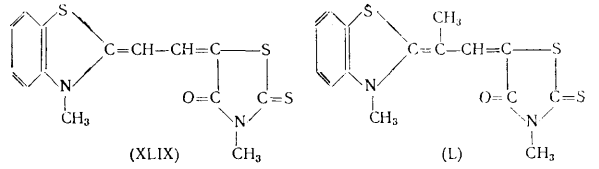
(XLVIII*a*) (XLVIII*b*)

and the following displacements of the absorption maxima, as compared with (XLVII), are observed:

in water	-65 mμ	in acetone	+ 4 mμ
in methanol	-43 mμ	in chloroform	+12 mμ.

Just these effects would be expected. The structure of (XLVIII) in water approaches the dipolar form (XLVIII*a*), and there is rotation of the ring about a single bond, causing a strong hypsochromic displacement of the absorption maximum. In methanol the order of the –C–C– bond in the molecule of (XLVIII) is higher, and the hypsochromic displacement is correspondingly less. In acetone the order of the bond is still higher, and the rotation of the ring has practically no influence on the absorption. In chloroform the bond order is ~ 1.5 (or more), and there is a marked bathochromic shift. The extinction of (XLVIII) in all solvents is much lower than that of (XLVII).

The destruction of the coplanarity of rings in the molecule of a dye exhibiting positive solvatochromism gives a different effect. If the absorption maxima of the planar (XLIX) and non-planar (L) merocyanines



(XLIX) (L)

are compared, it is seen that the destruction of the planar structure leads to a bathochromic shift of the maximum in all solvents:

in methanol	+4 mμ	in chloroform	+8 mμ
in acetone	+4 mμ	in benzene	+9 mμ.

This would be expected, since in this case there is free rotation in all the solvents about a bond of order approximately two.

The absorption maxima of (XLVII) and (XLVIII) in mixtures of pyridine and water of varying composition have also been compared. The displacements of the maxima were as follows:

in	80% pyridine	-24 mμ
	85% "	-18 mμ
	90% "	- 6 mμ
	95% "	- 1 mμ
	100% "	+ 7 mμ.

The transition from the hypsochromic effect, caused by rotation of the benzothiazole ring, to the bathochromic effect takes place at a pyridine concentration of ~ 95%. This is just the region in which, according to Brooker[8], the isoenergetic point of (XLVII) (in 92.5% pyridine) is found.

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ANALYSIS AND SEPARATION OF AROMATIC HYDROCARBONS BY GAS–LIQUID CHROMATOGRAPHY

V. I. Dal' and V. M. Nabivach

The rapid development of gas–liquid chromatography since 1952, when it was introduced by James and Martin, is undoubtedly due to its high analytical precision, to its speedy and reliable separations, and to the ease with which it can be applied to the automatic control of industrial processes.

The separation of a mixture in gas–liquid chromatography arises from the different rates of motion of the components along the layer of stationary phase, resulting in the formation of separate zones or bands. Thus the rate of movement of the bands and the dependence of band width on various experimental parameters form the main subject of the theory of gas chromatography[1-22]. The theories which have been put forward to explain the motion and the spreading of bands fall into three distinct groups. The first group includes the theory of theoretical plates[23-33], which discusses the chromatographic column as a plurality of elementary sections (theoretical plates), in each of which an equilibrium between the liquid and the gas is set up. No such equilibrium can exist in practice, whatever the length of column considered. The second group includes the various kinetic approaches[34-39] to the chromatographic process, based on considerations of molecular motions. These leave out of the picture all macroscopic characteristics. The third group is called the "theory of rates" or "theory of macroscopic constants"[40-46] and appears to be the most rational of the three. It describes the spreading of bands in terms of macroscopic parameters, such as diffusion coefficients, mass-transfer coefficients, etc.

Many articles and monographs have been devoted to the effects of particular factors on the efficiency of separation[47-72,235], and much attention has been given to the use of gas chromatography in the separation and analysis of various classes of organic compounds: saturated and unsaturated hydrocarbons[73-84], halogenated compounds[85-88], phenols[89-92], sulphur compounds[93-95], fatty acids and esters[96-99], amino and nitro compounds[100-105], lubricating oils[106-107], pyridine bases[108-109], products from oil refin-

ing[110-113], low-boiling gases[114-116], and others[117-121].

The most complex mixtures, and the most difficult to separate, are encountered in the petroleum and petro-chemicals industries. Among these must be included mixtures of aromatic hydrocarbons, and many publications have been devoted to the analysis and separation of such mixtures[122-146].

The growing volume of production of synthetic materials demands continuous improvements in the efficiency of the methods for producing raw materials, such as *p*-xylene. In this connection the gas–chromatographic separation and analysis of the xylene isomers offers an accurate and progressive method, which enables substances boiling within 0.1° of each other to be separated.

A detailed discussion of recent publications on the separation of the isomers of xylene will be given below.

Keulemans, Kwantes, and Zaal, in their study[147] of the influence of the stationary phase on the selectivity with which various hydrocarbons, including aromatics, were separated, found that fluorene picrate was highly selective towards aromatic compounds. This may be due to the formation of a molecular complex or of a primary addition product between solvent and solute in a picric acid–fluorene solution. The effect of temperature on the separation of *m*- and *p*-xylene was investigated by Vaughan[148], who showed that the separation was improved by lowering the temperature from 140° to 60°. Jentzsch and Bergmann[149] studied the relation between relative retention times and relative vapour pressures for a mixture of aromatic hydrocarbons containing xylene isomers. Whitham[150] analysed industrial xylene in a column packed with a stationary phase of fluorene picrate. Zlatkis, O'Brien, and Scholly[151] used a stationary phase of benzyldiphenyl in their analysis of aromatic hydrocarbons. Langer, Zahn, and Pantazoplos[152], who also separated the isomers of xylene, took advantage of the difference in their coordination electron-transfer behaviour, which involves "charge transfer" forces[153]. To this end, they used tetrahalogenophthalates, containing many electronegative substituents in the aromatic nucleus. As a result of the formation of complexes between the aromatic compounds and the substituted tetrahalogenophthalates[154,155], they succeeded in inverting the usual elution sequence, and detected *m*-xylene before the *p*-isomer. Zlatkis, Ling, and Kaufman[156] introduced many new polar compounds, such as 1-halogenonaphthalenes,

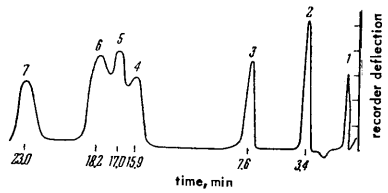


Fig. 1. Separation of aromatic hydrocarbons on a packed column[161]: 1) air; 2) benzene; 3) toluene; 4) ethylbenzene; 5) *p*-xylene; 6) *m*-xylene; 7) *o*-xylene.



Fig. 2. Separation of aromatic hydrocarbons on a capillary column[161]: 1) benzene; 2) toluene; 3) ethylbenzene; 4) *p*-xylene; 5) *m*-xylene; 6) *o*-xylene.

Separation of aromatic hydrocarbons by gas-liquid chromatography.

Composition of mixture to be Separated	Column dimensions (cm) and experimental temperature (°C)	Stationary phase	Flow rate of carrier gas	Sample size	Column efficiency in theoretical plates	Separation coefficient* for *m*- and *p*-xylene	References
Benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene	183×0.4 80°	dinonyl phthalate, 31%	N_2, 20 ml min^{-1}	10 μl			122
Acetone, n-octane, 2-methyloctane (isononane), benzene, ethylbenzene, toluene, *o*-, *m*-, *p*-xylene	180×0.6 120°	fluorene picrate, 28%	N_2, 33 ml min^{-1}				147
Benzene, cyclohexane, ethylbenzene, toluene, *o*-, *m*-, and *p*-xylene	330×0.4 78.6°	paraffin wax, 28%	N_2, 42 ml min^{-1}	0.5 mg	2000	1.008	126
Paraffins, ethylbenzene, *o*-, *m*-, and *p*-xylene	830×1.27 110°	fluorene picrate	N_2, 13.3 ml min^{-1}	0.5 ml	2000		150
Benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene	244×0.6 50°	1-chloronaphthalene, 15%	H_2, 220 ml min^{-1}		2500	1.060	156
Toluene, ethylbenzene, decane, *o*-, *m*-, and *p*-xylene	889×0.5 95°	di-n-propyl tetrachlorophthalate, 7%	He 84.8 ml min^{-1}	0.7 μl	7500	0.962	152
Benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene	500×0.5 100°	benzyldiphenyl, 15%	He 100 ml min^{-1}	0.005 ml	9500	1.032	151
Benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene	1200×0.025 78.5°	7,8-benzoquinoline	N_2 0.7 ml min^{-1}	1 μg	14600	1.030	161
Benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene	1524×0.22	poly(ethyl glycol dibenzoate), 5%	A	75 μg	30000		157
Ethylbenzene, *o*-, *m*-, and *p*-xylene	4572×0.025 70°	didecyl phthalate, 0.4%	0.43 ml min^{-1}		50000	1.021	159
Cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylene	5234×0.025 90°	poly(propylene glycol)	A_r 0.5 ml min^{-1}	100 μμl	100000	1.035	160

* The separation coefficient is defined as the ratio of the gas-retention volumes of the two components at the temperature of the experiment, and characterises the ease with which the components can be separated.

which afford a separation of *m*- and *p*-xylene when used as stationary phases. Scott[157] effected the complete separation of xylene isomers on a column of about 30 000 theoretical plates and over 15 m long. Franc and Jokl[158] carried out an analysis of xylenes in a mixture of aromatic hydrocarbons on an apparatus, called by them a spectrochromatograph, in which a gas–liquid chromatographic assembly was combined with a u.v. spectrophotometer. Golay[159] achieved a separation of *m*- and *p*-xylenes using a 45 m long capillary column, treated with didecyl phthalate. A 52 m capillary column, equivalent to 100 000 theoretical plates, was applied by Condon[160] to the same separation. Desty, Goldup, and Swanton[161] showed that 7,8-benzoquinoline offers better separation of the xylenes than the previously recommended stationary phases, such as squalane, tritolyl phosphate, and benzyldiphenyl. They carried out parallel separations of benzene, toluene, ethylbenzene, and the xylenes, on a column packed with 20% 7,8-benzoquinoline on kieselguhr, and on a 12 m capillary column, the walls of which were also lined with 7,8-benzoquinoline. Their results are shown in Figs.1 and 2. The choice of stationary phase for separating the isomers of xylene is also discussed elsewhere[162-164].

The conditions and experimental parameters for the analysis and separation of aromatic hydrocarbons are set out in the Table.

Mention should also be made of some interesting analyses and separations carried out on high-efficiency capillary columns[165-171]. Zlatkis and Haufman[172] have described a nylon capillary column, 1.6 km long and of ~ 0.2 cm internal diameter, whose efficiency exceeded 1 000 000 theoretical plates.

Various types of detector have been used for the quantitative and qualitative analysis of aromatic hydrocarbons[173]. In addition to the widely used thermal conductivity cell[150,151,174-176], the micro-flame detector[171-186] and its various modifications[187-189] receive frequent mention, as well as the ionisation detector, which measures the ionisation produced by β-radiation[190], the gas-density balance[191], the ordinary [argon (Ed. of Translation)] ionisation detector[192-196], a detector based on the absorption of u.v. light by the substance flowing through a spectrophotometer cell[197], the flame-ionisation detector[198], the vapour-phase i.r. spectroscopic method[199-201], and others[202-204].

Various foreign firms have produced chromatographic assemblies for the analysis of aromatic hydrocarbons, differing mainly in the type of detector used, the method of gas injection, the control of gas flow, and other details[205-214]. The British firm Shandon[215,216] market a chromatograph which incorporates a detector, designed by Scott[177], with a sensitivity (10^{-3}%) unaffected by the temperature of the experiment up to 375°. W.G. Pye and Co. (Cambridge, England) advertise an argon chromatograph based on Lovelock's ionisation detector[192]. The limit of detection of this instrument is as low as 10^{-11} mole, making its sensitivity tens of thousands of times higher than that of the thermal-conductivity cell. Separations of mixtures of benzene, toluene, ethylbenzene, and xylenes can be accomplished in 15 min on the apparatus marketed by the American firm Barber-Coleman Co.[218], whose ionisation detector relies on tritium as the source of ionisation.

The current trend towards extending gas–liquid chromatography to higher and higher temperatures[219-225] (300°, and even 500°) should enable close-boiling fractions to be separated for subsequent analysis by other methods[226,227].

Large-diameter columns have been built for the separation of moderately large quantities of mixtures of aromatic hydrocarbons on a preparative scale[129,228]. Atkinson and Tuey[229] used a 3 m column of 3 cm internal diameter to separate the constituents of a 30 g sample of purity better than 99.8 wt.%. Automatic methods of sample injection[230,231] and synchronised collection of the wanted fractions[232-234] will lead to practical processes for the gas–liquid chromatographic isolation of difficultly separable components of a mixture.

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STATISTICAL METHODS OF FINDING OPTIMUM CONDITIONS FOR A CHEMICAL PROCESS

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I. INTRODUCTION

Problems involving the determination of optimum conditions are frequently encountered in laboratory, pilot-plant, and full-scale studies. Many variables have to be tested in order to find the conditions giving the greatest yield, least cost, highest purity, etc. There is no point in setting out to test all possible combinations of the various factors in such a case, because the number of experiments required would be vast; even if that number were performed, the results from the first ones would not be comparable with those from the last on account of uncontrollable changes in the apparatus and in the reactants. Moreover, the results would be of little practical value, because we do not need to know the effects of the various factors in the yield for conditions far from the best.

In 1951 Box and Wilson[1] proposed a method of finding the best conditions by an application of mathematical statistics to the design of experiments and to the analysis of results. A few tests are made; the shortest route to the optimum region is deduced after each series even though the relation of the yield to the adjustable factors is not known in functional form. As the optimum region is approached, a larger series of tests is planned, and more elaborate methods of analysis are applied in order to deduce the best conditions. The conditions are interpreted by means of models in many-dimensional "factor" space. This method differs from ordinary ones in that the experiments are designed; the number of tests, and the places corresponding to those tests in factor space, are determined from certain mathematical rules. All factors are varied together; the approach is thus different from classical methods, in which only one factor is changed in each test. The differential

approach is also extremely important, because it enables one to perform only a few tests in the early stages in order to determine the direction that subsequent tests should take. The result is that many fewer tests are needed. Moreover, the information relates not merely to the main effects, but also to the effects of interactions (the latter effects are not deducible from the classical treatment). The final step is to formulate the results as an equation that serves to define the optimum conditions, which change in response to a number of factors, e.g. variation in the properties of the reactants. This method should find application to automatic chemical and metallurgical processes, although we know of no work that has yet been done on this topic.

In this review the method is illustrated by means of examples carried through to numerical calculations, and is presented in a form such that mathematical knowledge of undergraduate standard suffices to comprehend it. Familiarity with analysis of variance and regression analysis, and with matrix algebra, is required in order to make practical use of the method. Davies[2] gives a concise and convenient presentation of these subject in an appendix. Collaboration between a chemist and a mathematician is desirable; it is then sufficient for the chemist to be familiar with the basic ideas of the method, so that he speaks the same language as the mathematician. An ordinary calculating machine such as may be found in most laboratories will do for such calculations as are needed, though special machines can be used.

The Box-Wilson method is still under development, and methods of designing experiments are still being refined. There is as yet no practical handbook that covers the whole subject. Sufficient material is given here to illustrate the principles, although the examples do not incorporate the very latest suggestions. At the end a brief review is given of the uses of the method, together with a bibliography designed to fill any gaps.

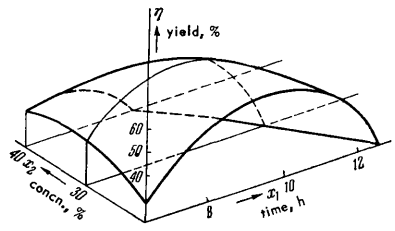


Fig. 1. The yield surface.

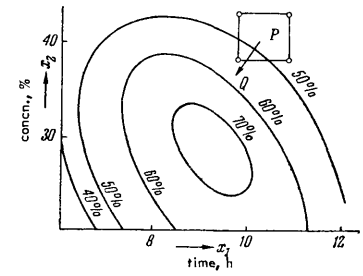


Fig. 2. Contour lines for the yield surface of Fig. 1 for a factorial experiment involving 2^2 tests.

II. DESCRIPTION OF THE METHOD †

Let us suppose that the yield η (or some other "response") depends on k quantitative factors x_1 to x_k. We call the function

$$\eta = \varphi(x_1, x_2, \ldots x_k)$$

the response function. If there are two independent variables, the function can be taken as the equation of a surface in three-dimensional space (Fig. 1). The surface can be represented on a plane as contours of equal yield, as in Fig. 2. Our problem is to pass from some point P to a point Q on a contour of higher yield. [We can use contour surfaces (Fig. 3) to represent the situation if there are three independent variables].

We can represent the response function for two independent variables by means of a terminated Taylor series (polynomial of degree n),

$$\eta = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{12} x_1 x_2 + \beta_{111} x_1^3 + \ldots, \qquad (1)$$

in which β_0 is the zero-order coefficient, β_1 and β_2 are the first-order coefficients, β_{ij} $(i, j = 1, 2)$ are the second-order coefficients, and so on. Now

$$\beta_1 = \frac{\partial \varphi}{\partial x_1}, \quad \beta_2 = \frac{\partial \varphi}{\partial x_2}, \quad \beta_{11} = \frac{1}{2}\frac{\partial^2 \varphi}{\partial x_1^2}, \quad \beta_{22} = \frac{1}{2}\frac{\partial^2 \varphi}{\partial x_2^2}, \text{ and } \beta_{12} = \frac{\partial^2 \varphi}{\partial x_1 \partial x_2}$$

The β are also called regression coefficients; here β_1 and β_2 are measures of the linear effects, β_{11} and β_{22} are measures of the quadratic effects, and β_{12} is a measure of the linear-linear interaction.

If we neglect the terms of second and higher orders in (1), we are left with the equation of a plane,

$$\eta = \beta_0 + \beta_1 x_1 + \beta_2 x_2,$$

in which β_1 represents the slope of the plane in the direction of the first variable, and β_2 does the same for the second variable. The surface may be approximated by means of a plane only in some bounded region far from a turning point.

The general principles used to find the maximum value of η may be illustrated as follows for the case of one independent variable, if we need take only terms up to the third order in (1). The least-squares method is used to find the parameters of the cubic giving the best fit, namely

$$Y = b_0 + b_1 x_1 + b_{11} x_1^2 + b_{111} x_1^3, \qquad (2)$$

in which Y is calculated from (2) and differs both from the true value and from the experimentally observed y_i. We

† A shortened and revised version of chapter 11 of Davies's[2] book.

equate the first derivative to zero:

$$\frac{dY}{dx_1} = b_1 + 2b_{11}x_1 + 3b_{111}x_1^2 = 0. \qquad (3)$$

This equation gives us the x_1 corresponding to the peak. The process is readily extended to k independent variables.

In practice this implies a large number of tests; for example, if we wish to examine five factors each at four levels, we must perform $4^5 = 1024$ tests. Sequential analysis [26] enables us to reduce that number greatly; let us consider the case of two independent variables. We assume that the initial conditions correspond to a point P (Fig. 2) far from the peak. The surface near P can be represented as a plane specified by the coefficients b_1 and b_2, which are found (by means of the least-squares method) from a few tests made for conditions in the region of P. Then b_1 and b_2 indicate the conditions to be used in order to reach point Q, which corresponds to a higher yield. Fresh values of b_1 and b_2 are found for Q, and so on. The process becomes more and more troublesome as the peak is approached; a plane becomes an unsatisfactory approximation to the surface, because the second-order constants become more important. The method cannot locate the peak; all it can do is to bring us to the almost-stationary region, in which the b become comparable with the errors of the measurements. The position of the peak (if one exists) can be found from a few tests once that region has been reached. A special method (see below) is used for this purpose.

The above method is based on constructing tangent planes to the surface, not on delineating the surface itself; the results can be wrong if the surface has more than one peak, because the peak reached is determined by the position of the initial point. It is usually safe to suppose that the surface has only one peak; a second peak can arise only if the reaction mechanism alters fundamentally.

The almost-stationary region can take any of the four forms shown in Fig. 4. In a we have a maximum; in b moderate changes in x_1 and x_2 result in almost unchanged yields; in c the best yield is to be reached by decreasing x_1 and increasing x_2; in d we have a saddle point.

On reaching an almost-stationary region our next task is to determine whether that region lies near a real peak (case a) or whether the case is b or c In case c we have to determine the direction of greatest slope, while in case d we have to find the direction corresponding to the maximum upward curvature This problem is solved by performing a second set of tests sufficient to define a quadratic representing the response surface.

The point in the almost-stationary region reached as a result of the first set is determined largely by the initial point, which may have to be taken at random. The point reached may be technically extremely inconvenient (the pressure or temperature may be too high, for example); then the second set of tests has as object to find a technically convenient point providing the optimum yield.

1. Determination of the Almost-Stationary Region

Let us suppose that we have a point O such that the surface near that point can be represented as a plane. We have to find the direction of the motion required to bring us to a point P such that the yield is as large as possible. It can be shown [1] that the direction is to be found by changing the independent variables in proportion to β_1, $\beta_2 \ldots \beta_k$; the direction is that of steepest ascent and lies at right angles

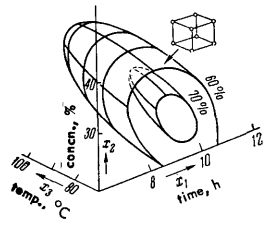


Fig. 3. Contour surfaces in three dimensional factor space for a 2^3 factorial experiment.

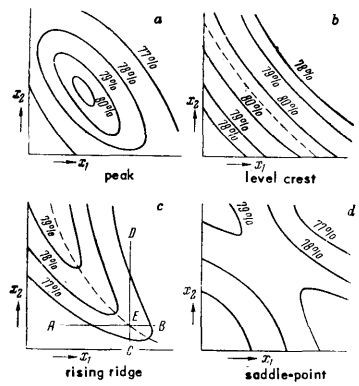


Fig. 4. Types of surface found in the almost-stationary region.

to the contour lines (surfaces).

In planning any such experiment, we must choose the amounts by which the factors are to be varied; this choice is made intuitively on the basis of previous experience. It is desirable to have the function as symmetrical as possible with respect to the factors. The number of tests is reduced very greatly if the levels are chosen properly.

Thus the first step is to determine the coefficients in

$$\eta = \beta_0 x_0 + \beta_1 x_1 + \beta_2 x_2 + \ldots \beta_k x_k, \qquad (4)$$

(The modified form for the constant term will be found to be convenient in what follows). Consider the case of three variables; each is used at two levels, which are denoted by +1 and -1; these symbols denote that the levels are centred on O, as shown in Fig. 5. Here there are $2^3 = 8$ tests to be made. Table 1 gives the levels to be used.

It is assumed that interactions are absent, so the number of tests can be halved; for example, we can take the

TABLE 1.

Tests	Levels		
	x_1	x_2	x_3
1	−1	−1	−1
*2**	1	−1	−1
*3**	−1	1	−1
4	1	1	1
*5**	−1	−1	1
6	1	−1	1
7	−1	1	1
*8**	1	1	1

TABLE 2.

Independent variables				Yield
x_0	x_1	x_2	x_3	
1	1	−1	−1	y_2
1	−1	1	−1	y_3
1	−1	−1	1	y_5
1	1	1	1	y_8

tests marked with an asterisk in Table 1 (solid circles in Fig. 5). Since Table 1 is orthogonal †, each coefficient b can be calculated separately; any one b is determined by summing the products of the y by the corresponding independent variable, and dividing this sum by the sum of squares for that variable. Let σ_y be the standard experimental error of y; then the variance of b, $\sigma^2\{b\}$, is found by dividing σ_y^2 by the sum of the squares of the corresponding independent variable

$$b = \Sigma yx/\Sigma x^2, \qquad \sigma^2\{b\} = \sigma_y^2/\Sigma x^2 \simeq s_y^2/\Sigma x^2, \tag{5}$$

in which s_y^2 is an estimate (see below) of σ_y^2. In particular, we can compile Table 2 for this example.

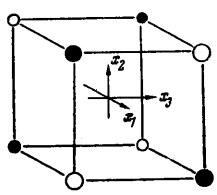


Fig. 5. Division of a complete 2^3 factorial experiment into two parts.

From the above formulae

$$\left.\begin{aligned} b_0 &= (1y_2 + 1y_3 + 1y_5 + 1y_8)/4 = \bar{y} \\ b_1 &= (1y_2 - 1y_3 - 1y_5 + 1y_8)/4 \\ &\cdots\cdots\cdots\cdots\cdots\cdots \\ &\cdots\cdots\cdots\cdots\cdots\cdots \\ \sigma^2\{b_0\} &= \sigma^2\{b_1\} = \sigma^2(b_2) = \sigma^2\{b_3\} = \frac{\sigma_y^2}{4} \end{aligned}\right\} \tag{6}$$

in which the b are estimates † of the β.

We now suppose that (4) is inadequate, being a linear approximation, and that we must include all second-order terms:

$$\eta = \beta_0 x_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3. \tag{7}$$

Table 3 shows how we may arrange the values for the independent variables in this equation.

We have only four tests, so we can find only four coefficients; but the second set of five columns merely repeats the first set, so we can put $b_0 \rightarrow \beta_0 + \beta_{11} + \beta_{22} + \beta_{33}$, in which the arrow denotes that the quantity on the left is an estimate of those on the right. Similarly, we have

$$b_1 \rightarrow \beta_1 + \beta_{23};\ b_2 \rightarrow \beta_2 + \beta_{13};\ b_3 \rightarrow \beta_3 + \beta_{12}.$$

The first expression may be interpreted as follows. If the surface is a plane, then b_0 (which equals $\bar{y}$) is an unbiassed estimate of the β_0, which corresponds to the centre of the area covered by the tests; but the estimate is biassed if the surface has a curvature. Again, β_{12}, β_{13}, and β_{23} are not zero if interactions occur, so b_1, b_2, and b_3 are biassed estimates of β_1, β_2, and β_3.

TABLE 3.

Independent variables										Yield
x_0	x_1	x_2	x_3	x_1^2	x_2^2	x_3^2	x_1x_2	x_1x_3	x_2x_3	
1	1	−1	−1	1	1	1	−1	−1	1	y_2
1	−1	1	−1	1	1	1	−1	1	−1	y_3
1	−1	−1	−1	1	1	1	1	−1	−1	y_5
1	1	1	1	1	1	1	1	1	1	y_8

TABLE 4.

Factor	Levels	
	−1	+1
x_1 (amount of solvent E, cm³)	200	250
x_2 (amount of C, mole/mole A)	4.0	4.5
x_3 (concentration of C, %)	90	93
x_4 (reaction time, h)	1	2
x_5 (amount of B, mole/mole A)	3.0	3.5

† Two linear functions

$$a_1x_1 + a_2x_2 \ldots + a_nx_n,$$
$$b_1x_1 + b_2x_2 \ldots + b_nx_n,$$

are said to be orthogonal if

$$a_1b_1 + a_2b_2 + \ldots a_nb_n = 0,$$

which is the condition for the absence of a linear dependence of the one function on the other. An orthogonal design is one in which the various effects are determined directly and separately. The sums of squares for all effects are then independent and additive.

† Few measurements are commonly made in any one research, and these may be treated as a random selection from some hypothetical population, which consists of all meaningful observations that might be made under those particular conditions. The statistical parameters calculated from the selections are treated as estimates of those parameters for the population. The estimates are traditionally denoted by Latin letters; the true parameters of the population by Greek letters. The estimate is termed unbiassed if it is free from systematic error.

TABLE 5.

Test	Levels					Yield y, %
	x_1	x_2	x_3	x_4	x_5	
1	−1	−1	−1	−1	−1	34.4
2	−1	−1	1	1	1	51.6
3	−1	1	−1	1	1	31.2
4	−1	1	1	−1	−1	45.4
5	1	−1	−1	1	−1	54.1
6	1	−1	1	−1	1	62.4
7	1	1	−1	−1	1	50.2
8	1	1	1	1	−1	58.6

These second-order effects must always be considered; the question will be discussed in detail in one of the examples given below.

Example. We have a reaction

$$A + B + C \rightarrow D + \text{other products},$$

which occurs in the presence of a solvent E; our object is to find the maximum yield of D for a given amount of A, which is the most expensive of the reactants and whose amount must remain fixed. Conditions are known that give 45% of the theoretical yield; the error of a single measurement is known to be 1% or less. Five factors are varied in Table 4; in planning the experiments, it is assumed that second-order effects are unimportant, so only $\frac{1}{4}$ of the total number of tests need be performed. On the other hand, theoretical considerations indicate that x_1 may interact with x_3, and this interaction was therefore isolated in the experimental design. Table 5 shows the plan of the tests; here we have the defining relations

$$x_4 = x_1x_2x_3 \text{ and } x_5 = -x_2x_3,$$

and further

$$1 = x_1^2 = x_2^2 = x_3^2 = x_4^2 = x_5^2 = x_1x_2x_3x_4 = -x_2x_3x_6 = -x_1x_4x_5.$$

Using (6) we get the estimates

$b_0 \rightarrow +\beta_0(+\beta_{11}^* + \beta_{22} + \beta_{33}^* + \beta_{11} + \beta_{55})$	48.5
$b_1 \rightarrow +\beta_1(-\beta_{15})$	7.9
$b_2 \rightarrow +\beta_2(-\beta_{25})$	−2.2
$b_3 \rightarrow +\beta_3(-\beta_{25})$	6.0
$b_{123} \rightarrow +\beta_4(-\beta_{15})$	0.4
$b_{23} \rightarrow +\beta_5(-\beta_{14} + \beta_{23})$	−0.4
$b_{13} \rightarrow 0(+\beta_{13}^* + \beta_{24})$	−1.8
$b_{12} \rightarrow 0(+\beta_{12} + \beta_{34})$	0.2

Assuming $\sigma = 1$, the standard error of the estimates is about 0.4. The asterisked quantities are ones corresponding to effects that might be expected on chemical grounds, and it is clear that b_{13} corresponds to a real effect (to a finite β_{13}). However, this is small relative to the first-order effects, so the linear approximation is adopted. Table 6 gives the derivation of the direction in which the greatest effect should be found.

The first line in Table 6 gives results for the base level; the second, those for unit change; the third, the coefficients b; the fourth, the product of unit change by the corresponding slope; the fifth, the changes in level corresponding to a change of 10 cm³ in x_1 for x_2 to x_5; the sixth, calculations for possible tests. Theoretical considerations indicate that a large increase in yield is to be expected, so test *9* is actually performed and gives a yield of 80%; test *10* gives 79.4%. It is difficult to attach much weight to this result, so a fresh series is planned with test *10* as the base point.

Before turning to the next stage, it should be pointed out that a failure to find any significant increase in yield in the first set of tests might be caused either by the effects that have been neglected or by experimental errors much larger than those anticipated. In either case the number of tests must be increased. It will be shown below how the first- and second-order effects may be determined simultaneously.

The unit changes may be adjusted as desired when the second set of tests is being designed. Two aspects have to be considered here.

1. Some effects appear small relative to others either because the base levels for those factors are close to the levels giving the maximum yield (certain other factors remaining unchanged), or because the unit changes are too small, or because the result is not dependent on those factors.

This situation can be clarified by means of increased unit changes; the yield is affected if the first two explanations apply, but there is no change if the last applies. In the experiment described above the result is not dependent on x_4 and x_5, so the unit changes for those factors are increased.

2. The unit changes for the factors x_1 to x_3 are chosen with due allowance for the facts that second-order effects become more important as the maximum is approached and that simultaneously the slopes become small and comparable with the experimental error. Any increase in the unit changes will tend to accentuate the first difficulty and to reduce the second. The effects of x_1 to x_3 are large in this case, and β_{13} is clearly finite, so it is decided to decrease the unit changes for those factors.

TABLE 6.

	x_1, cm³	x_2, mole	x_3, %	x_4, h	x_5, mole
Base level	225	4.25	91.5	1.5	3.25
Unit change	25	0.25	1.5	0.5	0.25
Coefficient b	7.9	−2.2	6.0	0.4	0.4
Unit change × b	197.5	−0.55	9.0	0.2	0.1
Change in level per 10 cm³ change in x_1	10	−0.028	0.456	0.010	0.005
	225	4.25	91.5	1.5	3.25
	235	4.22	92.0	1.5	3.25
	245	4.19	92.4	1.5	3.26
	255	4.17	92.9	1.5	3.26
Test 9	265	4.14	93.3	1.5	3.27
	275	4.11	93.8	1.6	3.27
Test 10	285	4.08	94.2	1.6	3.28
	295	4.06	94.7	1.6	3.28
	305	4.03	95.1	1.6	3.29

TABLE 7.

Factor	Levels	
	−1	+1
x_1 (amount of solvent E, cm³)	280	310
x_2 (amount of C, mole/mole A)	3.85	4.15
x_3 (concentration of C, %)	94	96
x_4 (reaction time, h)	2	4
x_5 (amount of B, mole/mole A)	3.5	5.5

TABLE 8.

Test	Levels					Yield y, %
	x_1	x_2	x_3	x_4	x_5	
11	−1	−1	−1	−1	1	77.1
12	−1	−1	1	1	1	69.0
13	−1	1	−1	1	−1	75.5
14	−1	1	1	−1	−1	72.6
15	1	−1	−1	1	−1	67.9
16	1	−1	1	−1	−1	68.4
17	1	1	−1	−1	1	71.5
18	1	1	1	1	1	63.4

Table 7 gives the levels used in the second set and Table 8 gives the design. Here we have

$$x_4 = x_1x_2x_3 \text{ and } x_5 = x_1x_2$$

and further

$$1 = x_1^2 = x_2^2 = x_3^2 = x_4^2 = x_5^2 = x_1x_2x_3x_4 = x_1x_2x_5 = x_3x_4x_5.$$

Some changes have been made in the design; here b_{12} has been used as an estimate of β_5, because the first set showed that the effects corresponding to β_{12} and β_{34} are absent. The calculated results are

$b_0 \rightarrow \beta_0 (+ \beta_{11} + \beta_{22} + \beta_{33} + \beta_{44} + \beta_{55})$	70.7
$b_1 \rightarrow \beta_1 (+ \beta_{25})$	−2.9
$b_2 \rightarrow \beta_2 (+ \beta_{15})$	0.1
$b_3 \rightarrow \beta_3 (+ \beta_{15})$	−2.3
$b_{123} \rightarrow \beta_4 (+ \beta_{35})$	−1.7
$b_{12} \rightarrow \beta_5 (+ \beta_{12} + \beta_{34})$	−0.4
$b_{13} \rightarrow 0 (+ \beta_{13} + \beta_{24})$	0.4
$b_{23} \rightarrow 0 (+ \beta_{23} + \beta_{14})$	−0.4

Assuming $\sigma = 1$, the standard error of the estimates is 0.4.

Here b_0 is larger than in the first set but less than in test *10*, so the surface must be curved. Coefficients β_{11}, β_{22}, etc. are negative near the peak, so b_0 underestimates β_0. Further, b_1 to b_3 have changed in sign, so the best point has been passed. The range of variation in x_4 is very different from that used in test *10*; the large negative value now found for β_4 indicates that the small value found previously was caused by the closeness to a conditional maximum, not by the absence of any effect. The sign indicates that we must return towards the earlier conditions. β_5 is still small, so it is clear that x_5 is not important.

Table 9 gives values calculated for further tests. The yields from tests *19* to *21* are 80.8, 84.0, and 81.5% respectively; the conditions of test *20* correspond to the almost-stationary region, and it was decided at this point to transfer the trials from the laboratory to a pilot plant.

2. Tests on the Almost-Stationary Region

The reaction is

$$A + B + C \rightarrow D + E + \text{other products.}$$

The objects here are to increase the yield of D and to decrease the yield of E (the product is useless if the proportion of E exceeds a certain level). The levels of variation are taken as the same for both factors. The initial yields are 64% for D and 15% for E; two sets of tests give 92% for D and less than 0.5% for E. Subsequently, a second series of tests was performed in order to maximise the yield of E; three sets raise it to 70%. The techniques used are those described above.

TABLE 9.

Test	x_1, g/cm³	x_2, mole	x_3, %	x_4, h	x_5, mole
19	295	4.0	95.0	3.0	4.5
	285	4.0	94.5	2.6	4.4
20	275	4.0	93.9	2.2	4.3
	265	4.0	93.4	1.8	4.2
21	255	4.0	92.8	1.4	4.1

TABLE 10.

Test	Levels		Yield y, %
	x_1	x_2	
1	−1	−1	71.7
2	0	−1	79.2
3	1	−1	80.1
4	−1	0	75.2
5	0	0	81.5
6	1	0	79.1
7	−1	1	76.3
8	0	1	80.2
9	1	1	75.8

TABLE 11.

Test	Independent variables						Yield y, %
	x_0	x_1	x_2	$x_1^2 - \frac{2}{3}$	$x_2^2 - \frac{2}{3}$	x_1x_2	
1	1	−1	−1	1/3	1/3	1	71.7
2	1	0	−1	−2/3	1/3	0	79.2
3	1	1	−1	1/3	1/3	−1	80.1
4	1	−1	0	1/3	−2/3	0	75.2
5	1	0	0	−2/3	−2/3	0	81.5
6	1	1	0	1/3	−2/3	0	79.1
7	1	−1	1	1/3	1/3	−1	76.3
8	1	0	1	−2/3	1/3	0	80.2
9	1	1	1	1/3	1/3	1	75.8

The nature of the surface must be established once the almost-stationary region has been reached. Let us suppose that there are two independent variables; the first- and second-order effects can be determined by means of 3^2 tests. The levels used are -1, 0, and +1; Table 10 gives the matrix used in designing the series. It is supposed that the surface can be represented adequately by the second-degree equation

$$\eta = \beta_0x_0 + \beta_1x_1 + \beta_2x_2 + \beta_{11}x_1^2 + \beta_{22}x_2^2 + \beta_{12}x_1x_2 \ldots \quad (8)$$

It is more convenient to use (8) in a slightly different form. The design of Table 10 has the following properties:

$$\sum x_1/n = \sum x_2/n = \sum x_1x_2/n = 0 ,$$

$$\sum x_1^2/n = \sum x_2^2/n = {}^2/_3 .$$

From (8) we find that the mean η, denoted by η_0, is given by

$$\eta_0 = \beta_0 + {}^2/_3\beta_{11} + {}^2/_3\beta_{22}.$$

We subtract this from (8) to get

$$\eta = \eta_0 x_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11}(x_1^2 - {}^2/_3) + \beta_{22}(x_2^2 - {}^2/_3) + \beta_{12} x_1 x_2 \ldots \quad (9)$$

The estimates are as before, except that b_0 (for β_0) is replaced by $\overline{y}$ (for η_0). We can find b_0 from

$$b_0 = \overline{y} - {}^2/_3 b_{11} - {}^2/_3 b_{22}. \quad (10)$$

Table 11 gives the values of the independent variables and the corresponding η. Now (9) implies that the sum of the products is zero for any two columns of independent variables. The orthogonality then gives us the simple expressions

$$\left.\begin{aligned} b &= \Sigma yx/\Sigma x^2 \\ \sigma^2\{b\} &= \sigma^2/\Sigma x^2 \end{aligned}\right\}, \quad (11)$$

and the sum of the squares (for the analysis of variance for the b) as

$$(\Sigma yx)^2/\Sigma x^2. \quad (12)$$

Table 12 gives the results; at the bottom we have the total sum of squares of the deviations, which is used in estimating the scatter of the observed quantities about the values predicted by the regression equation. There are three degrees of freedom, so the variance is $0.38/3 \simeq 0.13$. Here σ^2 is estimated as about 0.6 (from previous experience); this is larger than 0.13 (the residual variance), so we may assume that the experimental points fit adequately a second-degree equation †.

Now b_0 is

$$b_0 = 77.68 + (3.93 \times 0.67) + (1.38 \times 0.67) = 81.22.$$

The quantities are uncorrelated, so we have

$$\sigma^2\{b_0\} = \sigma^2\{y\} + \left(\frac{2}{3}\right)^2 \sigma^2\{b_{11}\} + \left(\frac{2}{3}\right)^2 \sigma^2\{b_{22}\} = 0.5555\sigma^2,$$

TABLE 12.

Constant	Σx^2	Σyx	$\Sigma yx/\Sigma x^2$	Degrees of freedom	$(\Sigma yx)^2/\Sigma x^2$	
η_0	9	699.1	77.68	1	54304.53	
β_1	6	11.8	1.97	1	23.21	
β_2	6	1.3	0.22	1	0.28	
β_{11}	2	— 7.87	— 3.93	1	30.97	78.10
β_{22}	2	— 2.77	— 1.38	1	3.84	
β_{12}	4	— 8.9	— 2.22	1	19.80	
Deviation from the regression line*			0.38			
Sum			54383.01			

* The regression equation is the equation relating one variable to the other variables under conditions in which random errors cause a spread in one or more of the variables.

† This statistical analysis may be illustrated by a simpler example. Let us suppose that we wish to construct a linear calibration graph from n quantities y_1 to x_n, which correspond to values x_1 to x_n. We find b_0 and b_1 by means of the least-squares method; it is usual to test for linearity at this stage by means of the F test (a test for the statistical significance of the variance ratio), which is used to compare the variance representing the scatter of the points about the line with the variance arising from experimental error. The assumption as to the linearity is justified if the ratio is statistically without significance. This means that the scatter is controlled solely by the errors of experiment, so a first regression equation represents the results adequately.

the final results being

$$b_0 = 82.22 \pm 0.58 \quad b_{11} = -3.93 \pm 0.55,$$
$$b_1 = 1.97 \pm 0.32 \quad b_{22} = -1.38 \pm 0.55,$$
$$b_2 = 0.22 \pm 0.32 \quad b_{12} = -2.22 \pm 0.39,$$
$$\sigma^2 = 0.6 \text{ (from previous experience).}$$

In particular b_2 does not differ significantly from zero, but we have no sufficient theoretical reason for putting β_2 equal to zero, so we adopt 0.22 as the best estimate of β_2.

Thus a quadratic equation gives an adequate description of the response function in the range covered by the tests:

$$Y = 81.22 + 1.97x_1 - 0.22x_2 - 3.93x_1^2 - 1.38x_2^2 - 2.22x_1x_2.$$

The figure corresponding to this equation is an ellipse; Fig. 6 shows the contours for $Y = 80\%$ and $Y = 75\%$. For any given x_1 we may find the x_2 corresponding to a particular yield, and so on.

A three-dimensional model may be used to interpret the behaviour of a system having three independent variables. No model can represent more complex cases; analysis of the equation (in canonical form) must suffice. When there are two variables, the canonical form is

$$Y - Y_S = B_{11}X_1^2 + B_{22}X_2^2. \quad (13)$$

This corresponds to placing the origin at S and to replacing the x_1 and x_2 axes by axes X_1 and X_2. Here Y_S is the yield at S (the peak). The case considered above gives us the canonical equation

$$Y - 81.49 = -4.35X_1^2 - 0.96X_2^2$$

whose centre lies at (0.30, 0.16) (see Fig. 6).

The equation has the following meaning. The change in the yield associated with any deviation from S is given by the right-hand side of the equation; here the two coefficients on that side are negative, so any displacement from S is associated with a fall in the yield (S is in fact the peak). Fig. 7 shows the four cases that are met with in practice, namely a peak, a ridge with a level crest, a rising ridge, and a saddle point. The first is considered above; the two coefficients are negative, and the centre corresponds to the best yield. The ellipse is elongated along X_2 if $|B_{22}| < |B_{11}|$; if both coefficients are positive, the centre is a point of least yield. The saddle-point type occurs when B_{11} is negative and B_{22} is positive; the contours are then hyperbolae, and their elongation depends on the ratio of the B ($|B_{11}| > |B_{22}|$ in Fig. 6). The level-crest

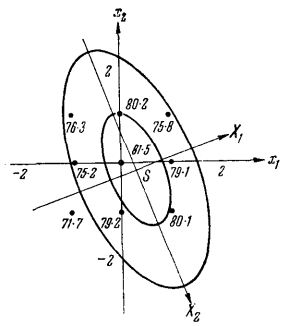


Fig. 6. The 80% and 75% ellipses and the experimentally observed yields.

type occurs if B_{11} is negative and B_{22} is zero; it forms a a common limit to the two previous types (elongation along X_2 indefinitely great). There is no unique point of best yield, but instead there is a line of best yield coincident with the X_2 axis. The equation is

$$Y - Y_S = B_{11}X_{11}^2 \qquad (14)$$

in which Y_S is the yield at any point on the X_2 axis.

The rising-ridge type occurs when the centre lies at infinity on X_2; B_{11} is negative, and any contour line is a parabola. The equation referred to an origin at any suitable point on the X_2 axis is

$$Y - Y_S = B_{11}X_1^2 + B_2X_2.$$

Here B_2 is the rate at which the yield increases, i.e. the slope, along the X_2 axis. This type is also a common limit to the first and last types; the centre is at infinity.

Only the first and last types are at all probable in practice; a case apparently of the second type is almost certainly one in which B_{22} has some small positive or negative value, so the contour lines are really curves greatly elongated along the X_2 axis, although the curvature may not be apparent. Again, it is very unlikely that the centre lies at infinity; an apparent third type is actually one in which the centre lies outside the region covered by the experiments.

The X_1 and X_2 axes will be turned relative to the x_1 and x_2 axes if $b_{12} \neq 0$, so the highest value obtained by varying x_1 will depend on the value assigned to x_2. Due allowance must be made for b_{11} and b_{22} in interpreting interaction effects.

Any equation obtained in this way is an adequate approximation to the response surface only in the neighbourhood of the region covered by the experiments. Analysis may show that the peak lies outside that region, in which case the previous tests have brought us to the area of a rising ridge. It may be impossible to draw any conclusion about the position or existence of a remote peak; attention must be devoted to the local ridge, which must form the subject of further tests.

As a second example we consider the case of a rising ridge. Assume that we have obtained an equation

$$Y - 60.64 = 3.672x_1 + 11.661x_2 - 3.514x_1^2 - 0.924x_2^2 + 2.220x_1x_2.$$

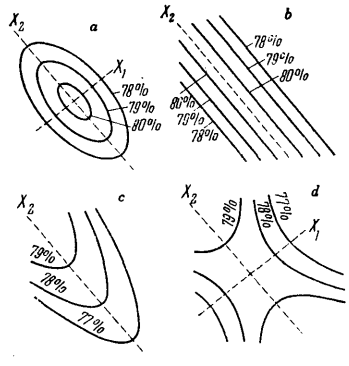


Fig. 7. Systems of contour lines for second-degree equations with two variables.

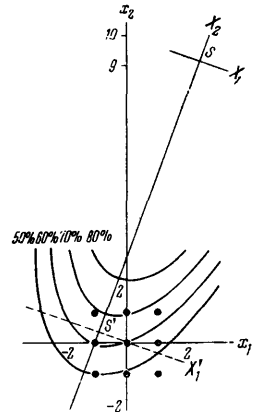


Fig. 8. Canonical representation of the region of a rising ridge (two variables).

The coordinates of S, and the predicted Y_S, are

$$x_{1S} = 2.370; \quad x_{2S} = 9.157; \quad Y_S = 109.68\%,$$

the canonical equation being

$$Y - 109.68 = 3.925X_1^2 - 0.513X_1^2,$$

and the equations relating X_1 and X_2 to x_1 and x_2 being

$$X_1 = 0.938(x_1 - 2.370) - 0.348(x_2 - 9.157),$$
$$X_2 = 0.348(x_1 - 2.370) + 0.938(x_2 - 9.157),$$

The contour lines are ellipses elongated along X_2, the maximum yield being at S; but that point is very far distant from O (the centre of the tests), so no conclusion can be drawn about the surface near S. The predicted Y_S is about 110%, which is clearly impossible. All the same, the equation represents the region near O quite adequately, and that region is the one of interest to us. Let us treat the problem in terms of the coordinates X_1 and X_2; with $x_1 = x_2 = 0$ we have the coordinates of O as

$$X_1 = 0.964; \quad X_2 = -9.414.$$

These are the shortest distances from O to the X_2 and X_1 axes respectively; the X_2 axis passes near O, and B_{22} is small, so the contour lines are drawn out in the direction of that axis. The conclusion is that we are in the neighbourhood of a rising ridge, whose direction lies parallel to the X_2 axis. We refer the canonical equation to a new origin S' whose coordinates are $X_1 = 0$, $X_2 = -9.414$ (this is the point on the ridge closest to O). In the new coordinate system

$$X_1' = X_1; \quad X_2' = X_2 + 9.414.$$

The X_1 and X_2 given by these expressions are inserted in the canonical equation to refer it to the new origin S':

$$Y - 64.22 = -3.925X_1'^2 - 0.513X_2'^2 + 9.659X_2'.$$

Here 9.659 is a measure of the slope of the crest, which is steep, so the next step is to follow the X_2' axis in the direction of increasing yield. Fig. 8 illustrates the situation; no such illustration can be given if the variables are numerous, but the canonical form often serves to elucidate the nature of the case.

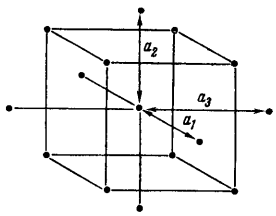


Fig. 9. Three-factor composite design.

TABLE 13.

Test	Levels			Test	Levels		
	x_1	x_2	x_3		x_1	x_2	x_3
1	−1	−1	−1	9	$-\alpha_1$	0	0
2	1	−1	−1	10	α_1	0	0
3	−1	1	−1	11	0	$-\alpha_2$	0
4	1	1	−1	12	0	α_2	0
5	−1	−1	1	13	0	0	$-\alpha_3$
6	1	−1	1	14	0	0	α_3
7	−1	1	1	15	0	0	0
8	1	1	1				

TABLE 14.

	Number of factors, k			
	2	3	4	5
Basic experiment (two levels)	2^2	2^3	2^4	$2^5_{/2}$ $(x_1x_2x_3x_4x_5=1)$
No. of extra points, $2k+1$	5	7	9	11
Distances of axial points from centre	1.000	1.215	1.414	1.547

3. Several Independent Variables

If the number of factors k is greater than two, the number of tests to be made is n^k (n is the number of levels), which is much larger than the number of independent variables. For example, if $k = 4$ and $n = 3$ we need $3^4 = 81$ tests in the usual factorial design, although first- and second-order effects are determined by only 15 quantities:

	Order	Number
β_0 (yield at the centre)	0	1
β_1 to β_4 (linear effects)	1	4
β_{11} to β_{44} (square-law effects)	2	4
β_{ij} ($i, j = 1$ to 4, $i \neq j$; interactions)	2	6
Total		15

The number of tests can be reduced by means of a composite design †. This design is effected as follows. Firstly, the entire system is tested at two levels in order to determine all first-order and interaction effects; then extra tests are made to establish the square-law effects.

Let us suppose that $k = 3$; here 2^3 tests are needed. If effects of order higher than the second are negligible, we can take b_0 as an estimate of $\beta_0 + \Sigma\beta_{ii}$, while the β_i and β_{ij} ($i \neq j$) are estimates of the corresponding β, and b_{123} is an estimate of the errors of experiment. A further seven tests are used to find the β_{ii}; one of these tests lies at the centre and the others lie at points whose coordinates are $\pm\alpha_1$, $\pm\alpha_2$, $\pm\alpha_3$. Table 13 gives the matrix for the design; the first eight points correspond to the 2^3 tests, the next six are those displaced from the centre, and the last is the one at the centre. Fig. 9 shows the arrangement. In general, for k factors we need an extra $2k + 1$ points, of which $2k$ are displaced (lie at $\pm\alpha_1 \ldots \pm\alpha_k$) and one lies at the centre.

This design enables us to use sequential methods. If the first set of tests shows that the first-order effects are large and that the interaction effects are slight, the extra tests are not needed; the method of steepest ascent is applied. On the other hand, the extra points are needed if second-order effects are to be allowed for.

The design may be orthogonal by giving all the α ($\alpha_1 \ldots \alpha_k$) a suitably chosen value, α. Table 14 illustrates orthogonal designs for two, three, and four factors. The second row covers the basic design for two levels, which involves $2^5/_2$ tests for five factors (here $x_1x_2x_3x_4x_5 = 1$); the design in that case involves a total of 2^4 tests with the extra column $x_5 = x_1x_2x_3x_4$. The fourth line gives the α for the orthogonal design, which corresponds to 3^2 tests for $k = 2$.

Example. Suppose the basic levels are such that -1 and +1 correspond to 65° and 75°; then the test corresponding to the point $(\alpha, 0, 0)$ with $\alpha = -1.215$ will fall at $70° - (5 \times 1.215) = 63.9°$.

We have to find the coefficients in the equation

$$\eta = \beta_0x_0 + \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \beta_{11}x_1^2 + \beta_{22}x_2^2 + \beta_{33}x_3^2 + \beta_{12}x_1x_2 + \beta_{13}x_1x_3 + \beta_{23}x_2x_3 \quad (16)$$

which we put in the more convenient form

$$\eta = \eta_0x_0 + \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \beta_{11}x_{11} + \beta_{22}x_{22} + \beta_{33}x_{33} + \beta_{12}x_1x_2 + \beta_{13}x_1x_3 + \beta_{23}x_2x_3 \quad (17)$$

in which $x_{11} = x_1^2 - \Sigma x_1^2/n$, etc. The estimates so obtained are as before, except that β_0 is found not directly but via the relation

$$b_0 = \overline{y} - b_{11}\Sigma x_1^2/n - b_{22}\Sigma x_2^2/n - b_{33}\Sigma x_3^2/n. \quad (18)$$

The sum of products between any two columns in the table of independent variables is zero if the equation is in this form and if $\alpha = 1.215$. The coefficients are found as before; we take the sum of the products of the responses by the elements of the corresponding independent variable and divide by the sum of squares of the elements of the independent variable.

Three-dimensional contour surfaces are readily derived by generalising from the two-dimensional contour lines; for example, A of Fig. 10 is a surface for which B_{11}, B_{22}, and B_{23} are negative (the figure is an ellipsoid of revolution). Here there is a point of maximum yield. Surface B is an elliptic cylinder, with B_{11} and B_{22} negative (B_{33} is zero).

† A composite design is one in which the number of tests is made not very much larger than the number of quantities to be determined (including in those quantities all second-order terms).

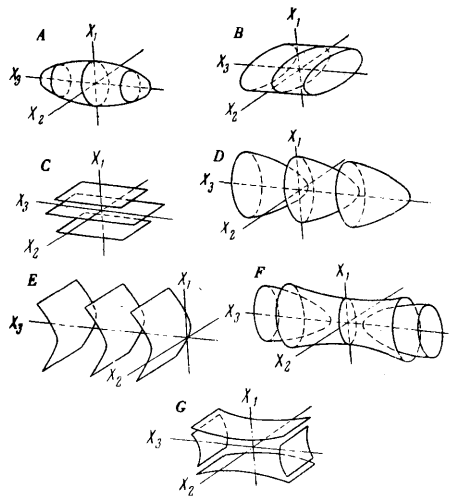


Fig. 10. Some three-dimensional contour surfaces for the almost-stationary region.

TABLE 15.

Factor	Levels −1	Levels +1	Base level	Unit change
T, °C	142	152	147	5
c, concentration of A, %	35	40	37.5	2.5
t, h	7	10	8.5	1.5

TABLE 16.

Test	Levels x_1	Levels x_2	Levels x_3	Yield y, %
1	−1	−1	−1	55.9
2	−1	−1	1	63.3
3	−1	1	−1	67.5
4	−1	1	1	68.8
5	1	−1	−1	70.6
6	1	−1	1	68.0
7	1	1	−1	63.6
8	1	1	1	62.4

TABLE 17.

Factor	Levels −2	Levels 0	Levels 2
T, °C	137	147	157
c, %	32.5	37.5	42.5
t, h	5 5	8.5	11.5

The X_3 axis is the line of maximum yield (a stationary one-dimensional level). Any deviation from that line results in a fall in the yield. Surface C is a plane parallel to the plane containing the X_2 and X_3 axes (a stationary two-dimensional level); here B_{22} and B_{33} are zero, and B_{11} is negative. Surface D is an elliptic paraboloid; the centre lies at infinity and B_{33} is zero. The origin may be displaced to a suitable point on the X_3 axis, whereupon the second-degree equation becomes:

$$Y - Y_S = B_{11}X_1^2 + B_{22}X_2^2 + B_3X_3, \qquad (19)$$

in which B_{11} and B_{22} are negative, B_{33} is zero, and B_3 is a measure of the slope of the crest along the X_3 axis. The system is equivalent to that of B, the only difference being that the crest is rising instead of level.

The reader can analyse the others for himself.

A good idea of the form of the surface may be obtained if one or more of the B are small relative to the others. The crest represents an almost-stationary region if the centre lies close to the region covered by the tests; but if the centre is far away, it is common to find that the ridge lies not far from the region covered by the tests, because the first-order coefficients will have been made small in the preceding sets of tests. In that case we select a new origin in order to determine the nature of the crest. Suppose B_{tt} is small relative to the others, for example; then the X_t axis represents the line of the crest, which passes near the experimental region. The new origin is taken near that region on the X_t axis; then the resulting equation contains a coefficient B_t, which will define the slope at the crest if the centre is far away. Again, B_{tt} and B_{ss} may both be small relative to the other B; then the plane of the X_t and X_s axes defines the plane of the ridge, which is likely to pass near the experimental region. The new origin is taken in that plane near the region; the new equation then contains coefficients B_t and B_s, which, if they are not small, point to a rising crest, whose slope may be determined as that of the line of steepest ascent.

Three variables. The reaction under investigation is of the type

$$A + B \rightarrow C + D;$$

the final product is a mixture of C and D with residual A and B. The problem is to obtain the best yield of C subject to the condition that the proportion of D must not exceed 20%. The factors that may be varied are the temperature (T), the initial concentration of A (c), and the reaction time (t); the initial amount of B is kept constant. A 2^3 factorial experiment is first performed; Table 15 gives the levels, the unit changes being

$$\left.\begin{aligned} x_1 &= (T - 147)/5 \\ x_2 &= (c - 37.5)/2.5 \\ x_3 &= (t - 8.5)/1.5 \end{aligned}\right\}. \qquad (20)$$

Table 16 gives the design and the results. The usual formulae lead to the following estimates:

b_0	$\rightarrow \beta_0 + \beta_{11} + \beta_{22} + \beta_{33}$	65.64 ± 0.4
b_1	$\rightarrow \beta_1$	1.76 ± 0.4
b_2	$\rightarrow \beta_2$	1.19 ± 0.4
b_3	$\rightarrow \beta_3$	-0.01 + 0.4
b_{12}	$\rightarrow \beta_{12}$	-3.09 ± 0.4
b_{13}	$\rightarrow \beta_{13}$	-2.19 ± 0.4
b_{23}	$\rightarrow \beta_{23}$	-1.21 ± 0.4
b_{123}	$\rightarrow 0$	(0.31 ± 0.4)

Previous experience indicates that the standard experimental error is about 1%. It is clear that the three interaction effects are large relative to the first-order effects, so no useful result is to be expected from the steepest-ascent method. Seven extra points with $\alpha = 2$ are added as in Table 17; the results are given in Table 18. The design is not completely orthogonal; α has been taken as two † in

† There is no point in making α greater than three, because the higher-order interactions then tend to become important.

order to reduce the variance of the second-order coefficients. The design is orthogonal for the first-order and interaction effects, so the coefficients for those effects are calculated as above [see (5)]. We find b_0, b_{11}, b_{22} and b_{33} from the equations:

$$\begin{aligned} 15b_0 + 16b_{11} + 16b_{22} + 16b_{33} &= 976.0, \\ 16b_0 + 40b_{11} + 8b_{22} + 8b_{33} &= 1014.3, \\ 16b_0 + 8b_{11} + 40b_{22} + 8b_{33} &= 1055.1, \\ 16b_0 + 8b_{11} + 8b_{22} + 40b_{33} &= 1041.9, \end{aligned}$$

which are best solved by matrix inversion; the usual methods give the reciprocal matrix as

$$\frac{1}{288}\begin{bmatrix} 224 & -64 & -64 & -64 \\ -64 & 26 & 17 & 17 \\ -64 & 17 & 26 & 17 \\ 64 & 17 & 17 & 26 \end{bmatrix}$$

whereupon the coefficients are found in the usual way. For example,

$$b_0 = (1/288)[(976 \times 224) - (64 \times 1014.3) - (64 \times 1055.1) - (64 \times 1041.9)]$$

and

$$\sigma^2\{b_0\} = (224/288)\,\sigma^2$$

Taking $\sigma^2 = 1$, we obtain $\sigma\{b_0\} = 0.9$. The final results are

$$\begin{aligned} b_0 &= 67.711 \pm 0.9 & b_{22} &= -0.264 \pm 0.3 \\ b_1 &= 1.944 \pm 0.3 & b_{33} &= -0.676 \pm 0.3 \\ b_2 &= 0.906 \pm 0.3 & b_{12} &= -3.088 \pm 0.4 \\ b_3 &= 1.096 \pm 0.3 & b_{13} &= -2.188 \pm 0.4 \\ b_{11} &= 1.539 \pm 0.3 & b_{23} &= -1.212 \pm 0.4 \end{aligned}$$

The estimate for the residual mean square is 4.85 (five degrees of freedom); this is larger than the expected value, but is not so large as to make the second-degree approximation inapplicable. If we take 4.85 as our measure of the variance due to experimental error, we must multiply the standard deviations of all the b by $\sqrt{4.85} = 2.20$.

The equation obtained,

$$Y = 67.711 + 1.944x_1 + 0.906x_2 + 1.069x_3 - 1.539x_1^2 - 0.264x_2^2 - 0.676x_3^2 - 3.088x_1x_2 - 2.188x_1x_3 - 1.212x_2x_3,$$

must be put in canonical form. The new origin at S is found by differentiating with respect to x_1, x_2, and x_3, and equating the derivatives to zero:

$$\begin{aligned} 2b_{11} + b_{12}x_2 + b_{13}x_3 &= -b_1, \\ b_{12}x_1 + 2b_{22}x_2 + b_{23}x_3 &= -b_2, \\ b_{12}x_1 + b_{23}x_2 + 2b_{33}x_3 &= -b_3. \end{aligned}$$

In the present case we have:

$$\begin{aligned} 3.078x_1 + 3.088x_2 + 2.188x_3 &= 1.944, \\ 3.088x_1 + 0.528x_2 + 1.212x_3 &= 0.906, \\ 2.188x_1 + 1.212x_2 + 1.352x_3 &= 1.069, \end{aligned}$$

and the solutions are

$$x_{1S} = 0.60; \quad x_{2S} = 0.215; \quad x_{3S} = 0.501.$$

These give $Y_S = 68.14$. Then we use (20) to revert to the ordinary units, whereupon the coordinates of the peak are found as 147.3°, 38.04% and 9.25 h.

The canonical form

$$Y - Y_S = B_{11}X_1^2 + B_{22}X_2^2 + B_{33}X_3^2$$

is derived by finding B_{11} to B_{33} from the characteristic equation

$$f(B) = \begin{vmatrix} b_{11} - B & \frac{1}{2}b_{12} & \frac{1}{2}b_{13} \\ \frac{1}{2}b_{12} & b_{22} - B & \frac{1}{2}b_{23} \\ \frac{1}{2}b_{13} & \frac{1}{2}b_{23} & b_{33} - B \end{vmatrix}$$

TABLE 18.

Test	Levels x_1	x_2	x_3	Yield, y, %
9	0	0	0	66.9
10	2	0	0	65.4
11	−2	0	0	56.9
12	0	2	0	67.5
13	0	−2	0	65.0
14	0	0	2	63.9
15	0	0	−2	60.3

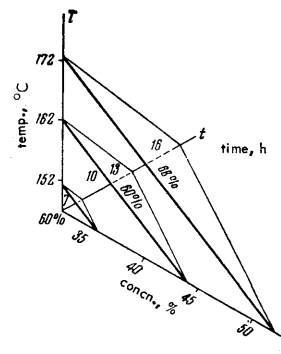


Fig. 11. Plane of almost-stationary yield (about 68%) and the planes for 60% yield.

or

$$f(B) = B^3 + \alpha B^2 + \beta B + \gamma = 0,$$

in which α, β, and γ are calculated from the known values of b_{11}, b_{12}, etc; the three roots are the coefficients in the canonical form. Here we have

$$B_{11} = -3.189, \quad B_{22} = -0.068, \quad B_{33} = 0.781.$$

The usual methods then give us the equations for the new coordinates in terms of the old as

$$\left.\begin{aligned} X_1 &= 0.7511(x_1 - x_{1S}) + 0.4884(x_2 - x_{2S}) + 0.4443(x_3 - x_{3S}) \\ X_2 &= 0.3066(x_1 - x_{1S}) + 0.3383(x_2 - x_{2S}) - 0.8897(x_3 - x_{3S}) \\ X_3 &= 0.5848(x_1 - x_{1S}) - 0.8044(x_2 - x_{2S}) - 0.1044(x_3 - x_{3S}) \end{aligned}\right\} \quad (21)$$

The canonical form is

$$Y - 68.14 = -3.190X_1^2 - 0.069X_2^2 + 0.780X_3^2\,\dagger,$$

in which B_{22} is negligible relative to B_{11} and B_{33}; it is not significantly different from zero. As B_{33} is positive, the yield should increase as we leave S in either direction along the X_3 axis, if the value is correct. Special tests do not confirm this prediction. The additional points are incorporated in further calculations, which show that B_{33} is also negligible relative to B_{11}, whose value is not essentially affected by the new results.

Neglecting B_{22} and B_{33}, we have the canonical form as

$$Y - 68.14 = -3.190X_1^2$$

† The coefficients in this equation are not exactly consistent with those given above. The same point occurs in Davies's book without explanation (Ed. of Translation).

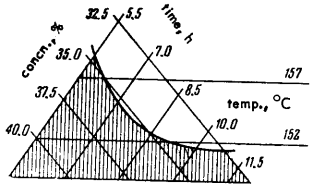


Fig. 12. Plane of greatest yield (about 68%) for product C. The yield of D is greater than 20% in the hatched region.

or

$$X_1 = \pm \sqrt{\frac{Y = 68.14}{-3.190}}.$$

This is the equation for a pair of planes; for $Y_S = 68.14$ we obtain the plane $X_1 = 0$, on which the yield is maximal at 68%. The first equation of (21) gives us the equation of this plane referred to the x coordinate system:

$$0.7511(x_1 - x_{1S}) + 0.4884(x_2 - x_{2S}) + 0.4443(x_3 - x_{3S}) = 0,$$

or in T, c, t, units,

$$0.1502\,T + 0.1954\,c + 0.2962\,t = 32.30.$$

This equation defines the various sets of conditions giving the same yield; Fig. 11 shows the plane of maximum yield and also the planes for $Y = 60$. We have here an illustration of the behaviour when the effects of a change in one variable are balanced out by changes in other variables. Fig. 11 gives a visual representation of the alternative conditions that lead to the same yield.

The next step is to find the conditions that make the yield (Z) of D less than 20%; we have to locate the region in the plane of maximum yield that has $Z < 20\%$. The second-degree equation obtained is

$$Z = 18.379 + 5.150x_1 + 2.362x_2 + 2.188x_3 + 0.728x_1^2 + 0.103x_2^2 + 1.303x_3^2 + 2.175x_1x_2 + 2.075x_1x_3 + 1.300x_2x_3.$$

This is transformed to the X coordinates; the values $X_1 = 0$ and $Z = 20$ are inserted, with the result

$$-0.855 = -0.319X_2 + 0.972X_3 + 0.380X_2^2 - 0.712X_3^2 + 0.079X_2X_3.$$

This equation defines the boundary for Z, (20% or more) on the surface of maximum yield, as shown in Fig. 12.

III. REVIEW OF APPLICATIONS OF THE BOX-WILSON METHOD

There are many examples of the use of this method in Great Britain and the USA; it is stated[3] that the American Cyanamid Company uses it to solve about half the chemical problems arising in its extensive research programme. The method has not yet been widely adopted, partly because the traditional training of chemists, metallurgists, or even physicists tends to neglect mathematical statistics.

The method has been expounded and illustrated in many books and papers[2,4,5]; three three-day seminars were devoted to the topic in the USA in 1956 and 1957[6]. Examples carried through to numerical calculations are presented in the mathematical literature in the abstract form illustrated above. Several such examples may be considered. Box and Youle[7] have examined a system that can be described in terms of two successive competing reactions

$$\left.\begin{aligned} 2a + bNb &\rightarrow aNb + ab \\ 2a + aNb &\rightarrow aNa + ab \end{aligned}\right\}, \qquad (22)$$

in which the initial compound bNb contains a large nucleus N bearing two groups b. The object is to maximise the yield of aNb by adjusting the temperature, reaction time, and concentrations. Baun and Schneider[3] have examined three problems, namely (1) a three-factor problem related to spray drying, (2) a problem of maximising the yield of the organic intermediate product in the reaction $A + B + C \rightarrow$ $\rightarrow$ product + intermediate product (here A/C and B/C are used as the independent variables), and (3) a reaction occurring in several reaction vessels arranged in series (here there were five factors, namely the concentrations of the reactants, a quality factor at two levels, and the effect caused by the use of reactors in series). Problems in chemical technology may be solved with reference to their economic aspects; for example, Box[8] has considered the technique of producing a compound C by fusing the reactants A and B; the factors were the temperature, the time of fusion, and the molar ratio of A to B, the effect being that on the cost of C, which is controlled by the yield of C and by the cost of performing the process. The cost of C is treated as a directly measurable dependent variable.

Problems have been considered in applied detail in certain journal articles; Morris and Bozalek[9] have used a response surface in studies of the accuracy of assays of sulphate in superphosphate, while Hackler et al.[10] have studied the uptake of water by fired whiteware compositions as a function of the composition (three factors) and of the firing temperature. Linear regression analysis has been applied[11] to the precipitation of $CaHPO_4$; four factors were used, namely the temperature, the concentrations of the reagents [$(NH_4)_2HPO_4$ and $CaCl_2$], and the rate at which the first reagent is added to the second. Li[12] has proposed a special table for representing the results of all steepest-ascent calculations in a standard form. One example of the use of this table is that of the choice of a composition for a complex-alloy steel in order to ensure the greatest resistance to fracture at high temperatures.

Applications have been made in organic chemistry, e.g. to the vapour-phase oxidation of naphthalene[13], to the emulsion polymerisation of vinyl chloride[14], and to the conditions for the best yield of 3-aminopropionitrile[15]. The Box-Wilson method has been combined with linear programming in order to optimise a catalytic cracking process[16]. The sealing strength of a wax-polyethylene blend used as a wrapping material has been examined[17].

Interesting applications have been found in biochemistry. The best values have been sought for the sodium citrate and glycerol concentrations and for the equilibration time in relation to the survival of bovine spermatozoa frozen at -79°[18]. A study has been made of the relationships between Cu, Fe, and Mo in the growth and nutrition of lettuce; the form of the nitrogen and the initial valence state of the iron were examined for their effects on the copper-dependent effects of the interaction and on the critical level of the copper[19,20]. The concentrations of Cu, Mo, and Fe giving the most rapid growth were determined.

It has not been possible to obtain some of the reports and conference proceedings listed below, and the contents can be judged only from the titles. For example, a study has been made of the flooding capacity of a pulsed column[21]; it has been pointed out[7] that here the experimental results have to be represented by a third-degree equation.

Whidden[22] deals with experimental design in metal processing; Shewell[23] deals with catalytic cracking, and so on.

Box and Wilson first presented the theoretical basis of their method in 1951[1]; subsequent developments[24] introduce the concept of the variance function, and in particular spherical variance functions. Since the location of the point of greatest yield (or other such point) is not known at the start, the experiment should be planned to make the variance of the predicted yield the same for all points at the same distance from the centre of the group of tests. Such designs are called "rotatable", because the orthogonal axes may take any orientation without effect on the confidence limits of the predicted yield. For these factors a central composite design is rotatable if the points lie at the corners of a cube and of an octahedron inscribed in the cube (Fig. 9), the coordinates of the corners of the octahedron being (±1.68, 0, 0), (0, ±1.68, 0), and (0, 0, ±1.68). Several examples of such designs have been given[4,5,19,20].

Box and Hunter[24] have considered rotatable experimental designs with satisfactory variance functions for their first- and second-degree polynomials and with independent variables numbering from two to infinity. Box and Draper[25] emphasize that a polynomial represents the real response surface only approximately; systematic errors accompany the random errors, and certain additional conditions are imposed on the design.

This new approach is complementary to the theoretical considerations commonly adopted by chemists. The general features of an experiment are established by selecting those factors that should be varied and the levels at which they are to be taken on the basis of general principles. However, those principles usually cannot predict precisely the conditions that will give the best yield, least cost, etc. The experimental work forms a link between the theory and the process; it has been called "creeping empiricism", because no general basis has yet been proposed for peak-seeking experiments. For example, the open-hearth process has been used in making steel for about a hundred years; much attention has been given to the theory of the process, but it is not possible to use theoretical considerations alone in designing a detailed programme suitable (say) for controlling the process by means of a computer. Between the theory and the finished steel there comes the steel worker, who uses his experience to interpret the information he receives during the melting and to find a means of performing the process in the best way. He has no formalised rules for interpreting the information and for reaching his conclusions, and their reliability cannot be assessed. The peak-seeking problem is solved intuitively; the theory of the open-hearth process indicates its general direction, but it cannot describe it fully. The same is true of any other complicated chemical process. The Box-Wilson method enables us to pass from intuitive methods to rigorously defined and mathematically sound ones.

The method may also be of use in solving certain theoretical problems in chemistry. Box and Youle[7] have examined the system described by (22) and have made an interesting comparison between the empirical response surface and the theoretical one. The first is obtained by fitting a polynomial to the experimental results; the second, by representing those results by means of a function derived from the general principles of reaction kinetics. Comparisons of this kind permit a more exact understanding of the mechanism of the process.

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CATALYSIS BY SALTS OF METALS OF VARIABLE OXIDATION STATE IN LIQUID-PHASE OXIDATION REACTIONS

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INTRODUCTION

The catalysis of the oxidation of organic substances by the addition of compounds of variable-valency metals is an important section of chemical kinetics. The mechanism of this catalysis includes elementary stages which are typical of ionic and radical reactions. We are therefore dealing with the border-land between the two most important types of chemical reactions: those in which ions take part, and free-radical processes. This type of catalysis has particular theoretical interest and practical significance for the stimulation of slow branched-chain reactions (processes with degenerate branching).

The catalysts normally used in the oxidation of hydrocarbons are the salts of organic acids with such metals as cobalt, manganese, iron, copper, chromium, lead, and nickel. The salt catalysts are widely used in laboratory practice and in various industrial processes. Potassium permanganate, for instance, is used as catalyst for the oxidation of paraffins by atmospheric oxygen in the production of fatty acids; cobalt and manganese acetates are used as catalysts for the oxidation of acetaldehyde to acetic acic and anhydride. The catalysts permit oxidation at a lower temperature, i.e., under milder conditions, and so decrease the development of more extensive oxidation processes. The study of the mechanism of such processes is also of undoubted interest in biochemistry, since such metals are components of many enzymes. For instance, the cytochromes (enzymes which take part in tissue respiration) contain iron.

A large number of investigations on the catalysis of liquid-phase oxidation reactions by metals of variable oxidation state have been reported in the last ten years. These experimental data provide the general outlines of the mechanism of the action of salt catalysts in the oxidation of aldehydes and hydrocarbons.

The acceleration of certain oxidation-reduction reactions by salts of iron and copper has long been known[1]. In 1931 Haber and Willstätter[2] based the mechanism of the action of ions of variable oxidation state on chain oxidation and decomposition reactions. They introduced the concept of the elementary reaction between the ion and the reacting compound, in which the oxidation state of the ion changes and a free radical is formed. This radical then commences the chain reaction. This mechanism was proved 20 years later by Bawn and coworkers[3-6] in the oxidation of aldehydes, which is catalysed by cobalt salts. The mechanism of salt catalysis proved much more complex in the oxidation reactions of hydrocarbons: after taking part in the oxidation reaction, the catalyst reacts with the oxidised products, causing the process to take place in several successive stages. Tsyskovskii and Kiseleva[7] showed that in the oxidation of kerosene, the catalyst accelerates the reaction only at its outset, and is then precipitated and does not

further affect the course of the oxidation. The present authors have studied the mechanism of the catalysis of the oxidation of n-decane and cyclohexane by cobalt and manganese salts[8-12].

In the absence of a catalyst, the autooxidation of hydrocarbons takes place by means of degenerate-branching chain reactions[13]. In the pure hydrocarbon free radicals may be formed by reaction with oxygen:

$$RH + O_2 \rightarrow R\cdot + HO_2^{\cdot},$$

$$2RH + O_2 \rightarrow 2R\cdot + H_2O_2.$$

Each radical causes a chain in which hydrocarbon and oxygen molecules form the hydroperoxide[14]:

$$R\cdot + O_2 \rightarrow RO_2^{\cdot},$$

$$RO_2^{\cdot} + RH \rightarrow ROOH + R\cdot.$$

With a dissolved-oxygen concentration greater than 10^{-3} M (when the partial pressure of oxygen is above 100 mm Hg) the radicals R· are very rapidly converted into peroxide radicals, so that $[R\cdot] \ll [RO_2^{\cdot}]$. The breaking of the chain therefore takes place as a result of collision and reaction between two peroxide radicals, e.g., by the reaction[15]

$$2R_1R_2CHOO\cdot \rightarrow R_1COR_2 + R_1R_2CHOH + O_2.$$

From time to time the hydroperoxide formed decomposes into free radicals by the reactions

$$ROOH \rightarrow RO\cdot + \dot{O}H,$$

$$2ROOH \rightarrow RO_2^{\cdot} + H_2O + RO\cdot.$$

At a sufficiently high temperature this method of formation of free radicals (degenerate branching of chains) becomes predominant in the reaction. When considering the action of catalysts on the oxidation of hydrocarbons, it is therefore necessary to bear in mind the possible occurrence of the above elementary reactions. The action of catalysts has a number of special features. The main property of a catalyst is its ability to initiate chains, i.e. to create free radicals in the reaction zone. It is also necessary to take into account the ability of the catalysts to break chains. There are cases where the action of catalysts may be likened to an initial "push" of the branched-chain process, after which the further presence of the catalyst in the reaction zone becomes unnecessary. There are also many cases where a change in the properties of the catalyst and the loss of its activity leads to a decrease in the rate of reaction. Sometimes the catalyst influences the composition of the oxidation products. The mechanisms of these phenomena will be reviewed here.

INITIATION OF CHAINS BY CATALYSTS

The uncatalysed oxidation of hydrocarbons usually proceeds with a self-accelerating effect and with a typical period of induction. Catalysts of variable oxidation state as a rule accelerate the oxidation and reduce the induction period, for instance cobalt, chromium, and manganese naphthenates in the oxidation of cyclohexane[16] and cobalt acetate in the oxidation of tetralin[17]. In the oxidation of cyclohexane in the presence of cobalt stearate at 130°, the more catalyst is introduced, the shorter the induction period[10]. Salt catalysts sometimes slow down the oxidation; these cases will be considered later.

The accelerating action of catalysts of variable oxidation state is due to their ability to generate free radicals. The

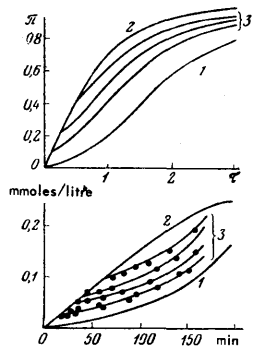


Fig. 1. Kinetic curves for the accumulation of the intermediate in oxidation: 1) without a catalyst; 2) with a catalyst; 3) with removal of the catalyst from the reaction zone. Upper figure — theoretical curves constructed from formulae (I) – (II) with $\omega_0 = 1$. Lower figure — kinetics of the accumulation of cyclohexanone at 130°, using 0.06 mole% of St_2Co.

direct participation of the catalyst in chain initiation is demonstrated by experiments in which the catalyst dissolved in the hydrocarbon is removed from the reaction zone[10] (the cobalt catalyst precipitates on cooling partially oxidised cyclohexane, and the oxidation continues after filtration).

Fig.1 shows kinetic curves for the accumulation of cyclohexanone (an intermediate in the oxidation of cyclohexane) in experiments in which the cobalt catalyst was removed from the reaction zone; after such removal, the rate of accumulation of cyclohexanone immediately falls. These results support the view that the catalyst is an agent which ensures a high rate of formation of free radicals. To demonstrate this, consider a simple mechanism for the oxidation as a degenerate-chain reaction with a single intermediate. Let the initial reactant RH be converted by a chain mechanism into the intermediate product P at a rate $k_2[RH]n$, where n is the concentration of free radicals. The product P decomposes by the chain mechanism at a rate $k_3[P]n$ and produces degenerate branching of the chains at a rate $k_4[P]$. The catalyst sets up a constant high rate of chain-initiation W_0. With quadratic termination of the chains, the stationary concentration of free radicals is

$$n = \left(\frac{W_0 + k_4[P]}{2k_6}\right)^{1/2},$$

where k_6 is the rate of quadratic termination of chains. The rate of accumulation of P in the presence of the catalyst is described by the differential equation

$$\frac{d[P]}{dt} = (k_2[RH] - k_3[P])\left(\frac{W_0 + k_4[P]}{2k_6}\right)^{1/2}.$$

Converting to dimensionless parameters, we obtain

$$\pi = \frac{k_3[P]}{k_2[RH]}, \qquad \tau = k_3\left(\frac{k_2k_4}{2k_3k_6}[RH]\right)^{1/2} t, \qquad \omega_0 = \frac{k_3W_0}{k_2k_4[RH]},$$

$$\frac{d\pi}{d\tau} = (1 - \pi)\sqrt{\omega_0 + \pi}.$$

Integrating this equation with the initial conditions $\pi = 0$ and $\tau = 0$, we obtain for the accumulation of P with time:

$$\tau = \left(\frac{Ae^{a\tau} - 1}{Ae^{a\tau} + 1}\right)a^2 - \omega_0, \qquad A = \frac{a + \sqrt{\omega_0}}{a - \sqrt{\omega_0}}, \qquad a = \sqrt{1 + \omega_0}. \quad \text{(I)}$$

In the absence of the catalyst, when $\omega_0 \cong 0$,

$$\frac{d\pi}{d\tau} = (1-\pi)\sqrt{\pi}, \qquad \pi = \left(\frac{e^{\tau}-1}{e^{\tau}+1}\right)^2. \qquad \text{(II)}$$

The removal of catalyst from the reaction zone at a time t is equivalent to saying that at the corresponding moment of dimensionless time τ, ω_0 becomes zero (more exactly, becomes very small). Up to time τ_1 the accumulation of P is described kinetically by formula (I), and from time τ_1, by the formula

$$\pi = \left(\frac{Be^{\tau}-1}{Be^{\tau}+1}\right)^2, \qquad B = \frac{\sqrt{1+\pi_1}+\sqrt{\pi_1}}{\sqrt{1-\pi_1}-\sqrt{\pi_1}}, \qquad \text{(III)}$$

which is obtained by integration of the equation

$$\frac{d\pi}{d\tau} = (1-\pi)\sqrt{\pi},$$

with the initial conditions $\tau = \tau_1$, $\pi = \pi_1$.

Fig.1 shows the kinetic curves for the accumulation of P constructed from formulae (I)–(III). The calculated results are in good agreement with experiment.

The rate of chain initiation can be measured by making use of strong liquid-phase oxidation inhibitors[18,19]. The inhibitor is added to the hydrocarbon, and the rate of formation of free radicals determined from the rate of disappearance of the inhibitor (which usually decomposes only by reaction with free radicals). In the oxidation of lubricating oil in the presence of iron and copper stearates, the use of inhibitors has shown[20] that the rate of chain initiation at the commencement of the reaction is directly proportional to the concentration of catalyst (at sufficiently low concentrations). At the start of the oxidation of cyclohexane, with a cobalt stearate concentration of 0.06 mole%, the rate of chain initiation is 4.7×10^{-7} mole litre^{-1} sec^{-1}.[21] In the absence of catalyst, and at a higher temperature, the initial rate of formation of chains in the oxidation of cyclohexane is much lower — 0.46×10^{-7} mole litre^{-1} sec^{-1}.[19] These results show that the catalysts accelerate the reaction by providing a high rate of formation of chains.

The mechanism of chain initiation by cobalt ions has been studied in detail in the oxidation of benzaldehyde in glacial acetic acid solution at room temperature with cobalt acetate as catalyst[5,6]. The rate of oxidation $V \propto [RCHO]^{3/2}[\text{catalyst}]^{1/2}$. The strong decelerating influence of added β-naphthol shows that the reaction is a chain process. With quadratic chain termination the velocity of the chain reaction must be $v = \text{const.}[RCHO]\sqrt{w_i}$, where w_i is the rate of formation of free radicals. Consequently, in the presence of the catalyst the rate of chain initiation must be proportional to $w_i \propto [RCHO][\text{catalyst}]$. Experiments with added inhibitor enabled the rate of chain initiation to be determined. It was found that $w_i = k_4[RCHO][\text{catalyst}]$ and $k_4 = 3 \times 10^9 \exp(-14{,}800/RT)$ litre mole^{-1} sec^{-1}. The kinetics of the reaction of Co^{3+} with benzaldehyde in acetic acid solution were studied in independent experiments in the absence of oxygen; the velocity constant found for the reaction of Co^{3+} with RCHO was practically identical with the velocity constant for chain initiation in the experiments with the inhibitor. This agreement proves conclusively that the chains are initiated by reaction of cobalt(III) with benzaldehyde. The mechanism of the catalysed oxidation of benzaldehyde is in entirely consistent with the scheme

$$RCO\cdot + O_2 \rightarrow RCOOO\cdot, \qquad (1)$$

$$RCOOO\cdot + RCHO \rightarrow RCOOOH + RC\dot{O}, \qquad (2)$$

$$Co^{2+} + RCOOOH \rightarrow Co^{3+} + OH^- + RCOO\cdot, \qquad (3)$$

$$Co^{3+} + RCHO \rightarrow Co^{2+} + RCO\cdot + H^+, \qquad (4)$$

$$Co^{3+} + RCOOOH \rightarrow Co^{2+} + RCOOO\cdot + H^+, \qquad (5)$$

$$2RCOOO\cdot \rightarrow \text{mol. products}. \qquad (6)$$

The perbenzoic acid formed by the oxidation oxidises the cobalt(II) to cobalt(III) in a fast step. The reaction between cobalt(III) and perbenzoic acid does not play any substantial part, since it takes place very slowly. The limiting stage in the cycle of cobalt oxidation–state changes is the reaction of cobalt(III) with the benzaldehyde. Each reaction involving a change in the oxidation state of the catalyst is accompanied by the formation of a free radical; the rate of chain initiation is, naturally, determined by the limiting stage, the reaction of cobalt(III) with the aldehyde. Under stationary conditions of initiation and termination of chains,

$$2k_4[Co^{+3}][RCHO] = 2k_6[RCO_3\cdot]^2,$$

$$[RCO_3\cdot] = \left(\frac{k_4[Co^{+3}][RCHO]}{k_6}\right)^{1/2},$$

$$v = k_2[RCHO][RCO_3\cdot] = \frac{k_2 k_4^{1/2}}{k_6^{1/2}}[RCHO]^{3/2}[Co^{3+}]^{1/2},$$

which is found experimentally.

The oxidation of acetaldehyde[4] differs from the oxidation of benzaldehyde in the formation of a peroxide X by the reaction

$$CH_3CHO + CH_3\overset{\overset{O}{\|}}{C}-OOH \rightleftarrows X$$

The peroxide X has been assigned the structure

$$CH_3-\underset{\displaystyle OOH}{\underset{|}{CH}}-O-\overset{\overset{O}{\|}}{C}-CH_3.$$

The equilibrium constant $K = \dfrac{[X]}{[CH_3CHO][CH_3COOOH]} = 0.3$ at 25°.

In the presence of catalysts (cobalt, manganese, and copper acetates) the peroxide X is rapidly decomposed, oxidising Co^{2+} and Mn^{2+} to Co^{3+} and Mn^{3+}. The rate of oxidation of acetaldehyde in acetic acid solution is $-\dfrac{d[O_2]}{dt} = k[CH_3CHO]^{3/2}[\text{catalyst}]^{1/2}[O_2]^0$, $k = 67$ litres mole^{-1} min^{-1} at 25°. As in the oxidation of benzaldehyde, the rate of chain initiation by the catalyst is limited by the reaction

$$Co^{3+} + CH_3CHO \rightarrow Co^{2+} + CH_3\dot{C}O + H^+.$$

Therefore

$$w_i = k_4[RCHO][Co^{3+}], \quad n = (k_4[RCHO][Co^{3+}]/k_6)^{1/2},$$

$$\frac{d[O_2]}{dt} = k_2[RCHO]\,n = k_2\sqrt{\frac{k_4}{k_6}}[RCHO]^{3/2}[Co^{3+}]^{1/2}.$$

The peroxide X reacts with the catalyst more rapidly than peracetic acid. The velocity constant for the reaction of Mn^{2+} with X at 25° is 10^3 litres mole^{-1} sec^{-1}, while for the reaction of Mn^{2+} with CH_3COOOH it is 61 litres mole^{-1} sec^{-1}.[4]

Woodward and Mesrobian[17] studied the oxidation of tetralin in acetic acid solution in the presence of cobalt acetate, and showed that the maximum concentration of hydroperoxide in this reaction is

$$[ROOH]_{max} \propto \left(\frac{[RH]}{[(CH_3COO)_2\cdot Co]}\right)^2,$$

and the maximum rate of absorption of oxygen,

$$-\frac{d[O_2]}{dt} \propto [RH]^2,$$

is independent of the concentration of catalyst. Experiments on the decomposition of the hydroperoxide in a nitrogen atmosphere showed that

$$-\frac{d\,[ROOH]}{dt} = k_3\,[ROOH]\,[(CH_3COO)_2Co]^2,$$

k_3 = 40 litre^2 mole^{-2} sec^{-1} at 81°. These facts agree well with the reaction mechanism proposed by the authors:

$$R\cdot + O_2 \rightarrow RO_2^{\cdot},$$

$$RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot}, \qquad (2)$$

$$ROOH + 2(CH_3COO)_2Co \rightarrow \text{free radical}, \qquad (3)$$

$$2RO_2^{\cdot} \rightarrow \text{mol. products}. \qquad (6)$$

According to this mechanism,

$$\frac{d\,[ROOH]}{dt} = k_2\,[RH]\,[RO_2\cdot] - k_3\,[ROOH]\,[Ac_2Co]^2,$$

$$[RO_2\cdot] = \left(\frac{k_3\,[ROOH]\,[Ac_2Co]^2}{2k_6}\right)^{1/2}, \quad [ROOH]_{max} = \frac{k_2^2\,[RH]^2}{2k_3k_6\,[Ac_2Co]^2},$$

$$-\left(\frac{d\,[O_2]}{dt}\right)_{max} = k_2\,[RH]\,[RO_2\cdot] = \frac{k_2^2\,[RH]^2}{2k_6}.$$

The relationships obtained from this mechanism agree with the experimental data. The energies of activation were obtained from the temperature variation of k_3 and $-(d[O_2]/dt)_{max}$: E_2 = 8.2 kcal mole^{-1} and E_3 = 23 kcal mole^{-1}.

The oxidation of aldehydes shows convincingly that the initiation of chains by salts of such metals is closely bound up with the change in their oxidation state. A change in oxidation state of cations such as those of cobalt and manganese has been observed in many studies of catalysed oxidation. Oxidation of cobalt(II) and manganese(II) is easily observed from the change of colour of their solutions. A solution of cobaltous stearate or naphthenate in a hydrocarbon is pale violet if the salt contains water of crystallisation, or pink if it is anhydrous. In a hydrocarbon which is being oxidised, the cobalt is converted to the +3-state, and the solution takes on an intense green colour[8,10,21-25]. The spectrum of cobalt(III) from an oxidised hydrocarbon is the same as the spectrum of a solution of pure cobaltic acetylacetonate[21,24]. The spectrum of cobalt (III) in solution in a hydrocarbon has an absorption maximum at 600 mμ, a minimum at 520 mμ, and strong absorption in the ultra-violet. Study of the kinetics of the accumulation of cobalt(III) in cyclohexane which is being oxidised has shown that not all of the cobalt is converted to the +3-state during the course of the reaction; the concentration of Co^{3+} reaches a maximum and then decreases (Fig. 2).

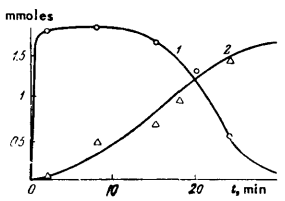


Fig. 2. Kinetic curves for the accumulation of 1) Co^{3+} and 2) hydroperoxide in the catalysed oxidation of cyclohexane (124°, 3 mmoles of cobalt stearate per litre).

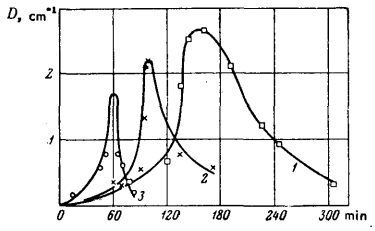


Fig. 3. Kinetics of accumulation of Mn^{3+} during the oxidation of n-decane with a catalyst concentration 0.012 M at: 1) 120°; 2) 130°; 3) 140°.

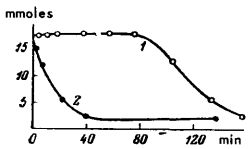


Fig. 4. Change of oxidation state of iron in the oxidation of cyclohexane: 1) at 110° with 0.018 mole% of St_3Fe; 2) at 130° with 0.017 mole% of St_2Fe.

A solution of a manganous salt in a hydrocarbon is colourless. During the oxidation a brown colour appears, typical of manganese in a higher oxidation state[7,8,21,24,26]. The spectrum of an oxidised manganese catalyst coincides with that of manganese(III) benzoate[24], and consequently manganese, like cobalt, is converted to the +3-state during the oxidation. The concentration of manganese(III) in the course of the oxidation of n-decane[26] passes through a maximum (Fig.3); the maximum concentration of Mn^{3+} is 20-30% of its total concentration of 0.012 moles per litre. Manganese is completely converted to the +3-state in the oxidation of cumene and tetralin[26]. This difference is due to the different composition of the oxidation products in these reactions and to their differing reducing action on Mn^{3+}.

A change in the oxidation state of iron in an oxidised hydrocarbon has been demonstrated[12] (Fig.4). The more rapid the oxidation (the higher the reaction temperature), the more rapid is the onset of the reduction of iron(III) to iron(II). This shows the close link between the formation of the oxidation products and the reduction of the catalyst. The reduction of copper(II) to copper(I) has been observed in the oxidation of decane[27].

The oxidation of aldehydes and observations on the catalysed oxidation of hydrocarbons and the reaction between salts of such metals and hydroperoxides indicate the close connection between oxidation–state changes of the catalysts and their part in chain initiation. It is often found that the start of a catalysed oxidation coincides with a change in the oxidation state of the catalyst, which is easily seen from

the change of colour of the solution. In the oxidation of acetaldehyde with manganese acetate[28], of branched-chain paraffins with cobalt stearate[22], and in the oxidation of decane[8], α-pinene[29], and cyclohexane[10] with cobalt stearate, it has been observed that the oxidation commences after an induction period, and coincides with a change in the oxidation state of the catalyst (with a rapid oxidation of Co^{2+} to Co^{3+} and of Mn^{2+} to Mn^{3+}).

In general, the one-electron transfer reaction between a molecule (a species of saturated valency) and a metal of variable oxidation state, must invariably lead to the formation of a free radical or atom. For example, in the reaction between cobalt(II) and a molecule A:B, cobalt(III) and a free radical or atom is formed:

$$Co^{2+} + A{:}B \rightarrow Co^{3+} + A\cdot + B^{-} \text{ (or } A^{-} + B\cdot).$$

An analogous effect is observed in the reverse transition of cobalt from the +3-state to the +2-state:

$$Co^{3+} + A{:}B \rightarrow Co^{2+} + A^{+} + B\cdot \text{ (or } A\cdot + B^{+}).$$

The classical example of oxidation-reduction reactions in which such cations participate are the reactions of peroxides with the ions of iron, copper, and cobalt. Since these reactions are closely related to the catalysed oxidation of hydrocarbons, they will be considered in more detail. Hydroperoxides are the primary molecular products of the oxidation of hydrocarbons, and play an important role in uncatalysed oxidation, since they ensure degenerate chain branching.

Of great significance also is the participation of hydroperoxides in catalysed oxidation reactions, in which reaction between a hydroperoxide and the catalyst is a powerful source of free radicals. A mechanism for the decomposition of peroxides by cations of variable oxidation state was first proposed by Haber and Weiss[30], with the decomposition of hydrogen peroxide in the presence of ferrous ions as an example. The primary elementary reaction between hydrogen peroxide and Fe^{2+} is

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + \cdot OH.$$

The resulting hydroxyl radical causes chain decomposition of the hydrogen peroxide; in the presence of a monomer (e.g. methyl methacrylate) the hydroxyl radicals cause radical polymerisation[31]. The velocity constant of the reaction between Fe^{2+} and H_2O_2 is $k = 1.8 \times 10^9 \exp(-10\,000/RT)$ litres mole^{-1} sec^{-1}.[31]

Hydroperoxides also decompose very rapidly in aqueous solution in the presence of iron ions, with the formation of alkoxy radicals:

$$Fe^{2+} + ROOH \rightarrow Fe^{3+} + OH^{-} + RO\cdot,$$

as was shown by Kharasch[32], who decomposed cumene, tetralin and t-butyl hydroperoxides with iron ions in the presence of butadiene; the reaction products included the compounds (A) and (B), formed by the addition of the alkoxy radical to a butadiene molecule, with subsequent recombination of the radicals:

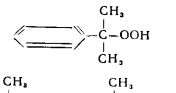
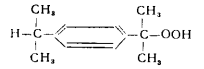
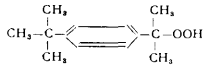
$$ROCH_2CH{=}CHCH_2CH_2CH{=}CHCH_2OR, \quad (A)$$

$$ROCH_2CH{=}CHCH_2CH(CH{=}CH_2)CH_2OR. \quad (B)$$

Table 1 gives the velocity constants for reactions of Fe^{2+} with ROOH[33,34].

The thermal decomposition of the hydroperoxides to form free radicals takes place with an energy of activation ~30 kcal/mole. The iron ions react with the hydroperoxides with much lower energies of activation of 10-12 kcal/mole. The rate of reaction of cumene hydroperoxide with Fe^{2+} relative to its rate of thermal decomposition at 100° is $4.1 \times 10^8[Fe^{2+}]$, i.e. with $[Fe^{2+}] = 10^{-5}$ M, the reaction between ROOH and Fe^{2+} is 4000 times as rapid as the thermal decomposition.

TABLE 1. Velocity constants for the reaction of Fe^{2+} with ROOH for some hydroperoxides.

Hydroperoxide	Velocity constant, litres mole^{-1} sec^{-1}
	1.07×10^{10} exp (−12 000/RT)
	4.0×10^{9} exp (−10 800/RT)
	1.8×10^{9} exp (−9900/RT)

In the oxidation of hydrocarbons the catalysis is not by ions, but by the molecules of salts of metals of variable oxidation state; therefore the reaction between the hydroperoxide and the catalyst takes place with the formation of a free radical and a new polar bond (and not an ion, as in aqueous solution), for example:

$$St_2Co + ROOH \rightarrow RO\cdot + St_2CoOH,$$

where St = n-$C_{17}H_{35}COO$.

This reaction apparently takes place more slowly than the analogous one in aqueous solution, but much faster than the thermal decomposition of the hydroperoxide. The rapid decomposition of hydroperoxides in solution in hydrocarbons in the presence of small amounts of the stearates or naphthenates of cobalt, manganese, and iron is well known, and the strong catalytic action of these salts on the decomposition of hydroperoxides is not open to doubt. However, the kinetics and mechanism of the catalysed decomposition of hydroperoxides in solution in hydrocarbons have been little studied. The kinetics of the reaction between manganese stearate and n-decyl hydroperoxide have been studied[35]; this reaction takes place very rapidly, with decomposition of the hydroperoxide and oxidation of part of the manganese(II) to manganese(III). The kinetic curves depicting the change of optical density of the reactants, indicating the formation of manganese(III) are shown in Fig.5. The amount of manganese oxidised to the +3-state is less than the quantity of hydroperoxide decomposed, but with increase of the ratio $a = \frac{[St_2Mn]_0}{[ROOH]_0}$, the ratio $b = \frac{[Mn^{3+}]}{[ROOH]_{decomp}}$ also increases: when $a = 3.23$, $b = 48\%$, and when $a = 9.7$, $b = 80\%$. In addition to the reaction between St_2Mn and ROOH, there is apparently an induced decomposition of the hydroperoxide also. The initial rate of oxidation of manganese(II) is $k\,[St_2Mn]\,[ROOH]$, where $k \cong 2.8 \times 10^{11} \exp(-18{,}000/RT)$ litres mole^{-1} sec^{-1}. At 90° $k = 4.1$ litres mole^{-1} sec^{-1}, while for the reaction between Fe^{2+} and ROOH in aqueous solution, $k = 910$ litres × moles^{-1} sec^{-1}. Since manganese is a more active cata-

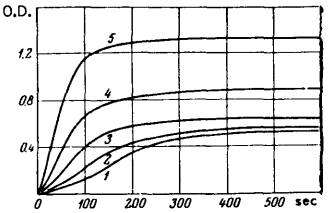


Fig. 5. Kinetic curves for the change of optical density of a solution of St_2Mn and n-decyl hydroperoxide in decane, showing the oxidation of the catalyst by the hydroperoxide at: 1) 80°; 2) 85°; 3) 90°; 4) 95°; 5) 104°. $[St_2Mn] = 4.86 \times 10^{-3}$ M, $[ROOH] = 1.56 \times 10^{-3}$ M.

lyst than iron, this difference must be due to the much greater reactivity of ions than of molecules of the organic-acid salts. However, the reactivity of such catalysts in the decomposition of hydroperoxides must still be considered as very high even in hydrocarbon solutions. For example, the rate of reaction of manganese stearate (0.01 M) with n-decyl hydroperoxide at 140° is 3.7×10^4 times the rate of decomposition of this hydroperoxide into free radicals in the decane being oxidised, where the velocity constant for the decomposition is $k = 6 \times 10^8 \exp(-24{,}000/RT)$ sec^{-1} [36]. In catalysis with ferric salts the catalyst first forms a complex with the hydroperoxide, which then decomposes to form free radicals[37,38]:

$$FeSt_3 + ROOH \rightleftarrows [FeSt_3 \ldots ROOH],$$

$$[FeSt_3 \ldots ROOH] \rightarrow FeSt_3 + RO\cdot + \cdot OH.$$

The formation of an analogous complex has been observed in the decomposition of ethylbenzene hydroperoxide in the presence of copper stearate[39].

This account has shown convincingly that the reaction between catalysts of variable oxidation state and hydroperoxides plays an important part in the mechanism of the catalysed oxidation of hydrocarbons.

Figs.3 and 4 show that in the hydrocarbon being oxidised, reduction of the oxidised form of the catalyst also occurs. It has been suggested that this takes place only as a result of reaction with the hydroperoxide;

$$St_2CoOH + ROOH \rightarrow St_2Co + RO_2\cdot + H_2O.$$

This reaction takes place in aqueous solutions[40], but it is much slower than the reaction between Co^{2+} and ROOH, and in fact takes place between the cobalt and hydroperoxide ions:

$$Co^{3+} + ROO^- \rightarrow Co^{2+} + RO_2\cdot.$$

In a hydrocarbon, where the hydroperoxide is known not to dissociate, this reaction takes place extremely slowly, if at all. Moreover, it does not explain the reduction of the catalyst to the lower oxidation state during the reaction, as the following kinetic calculation shows. Let us denote the reduced form of the catalyst by M^{2+} and the oxidised form by M^{3+}, and let us examine the kinetics of the accumulation of M^{3+} during the oxidation, assuming that both forms of the catalyst react only with the hydroperoxide. Let the catalyst be introduced at the commencement of the reaction in the lower oxidation state, M^{3+} being formed by reaction between M^{2+} and ROOH with a velocity constant k_3, and disappearing by reaction with ROOH with a velocity constant k_5. The rate of accumulation of M^{3+} is

$$\frac{d[M^{3+}]}{dt} = (k_3[M^{2+}] - k_5[M^{3+}])[ROOH].$$

$$\frac{dx}{dt} = (x_p - x)(k_3 + k_5)[ROOH], \text{ where } x = \frac{[M^{3+}]}{[M^{2+}]_0} \text{ and } x_p = \frac{k_3}{k_3 + k_5},$$

hence,

$$x = x_p\left(1 - e^{-\int_0^t (k_3 + k_5)[ROOH]\,dt}\right).$$

Irrespective of the actual form of the kinetic curve for the accumulation of the hydroperoxide, $\int_0^t [ROOH]\,dt > 0$ and increases with t. Consequently, in the course of this reaction, $x \rightarrow x_p$, and having reached this kinetic equilibrium value, remains constant, i.e. the concentration of M^{3+} in the course of the reaction cannot decrease. To obtain a concrete form of $x = x(t)$, let us assume that chain initiation during the oxidation occurs by reactions (3) and (5), for simplicity of calculation assuming that $k_3[M^{2+}] + k_5[M^{3+}] \cong k_3[M^{2+}]_0$, that chain termination is quadratic (velocity constant k_6), and that the loss of peroxide at the commencement of the reaction can be ignored. Then the rate of formation of hydroperoxide in this reaction will be

$$\frac{d[ROOH]}{dt} = k_2[RH]\left(\frac{k_3[M^{2+}]_0[ROOH]^{1/2}}{k_6}\right)$$

(k_2 relates to the reaction between $RO_2\cdot$ and RH),

$$[ROOH] = A\,t^2, \quad A = \frac{k_2^2 k_3[RH]^2[M^{2+}]_0}{k_6},$$

and for the accumulation of the oxidised form of the catalyst we have the formula

$$x = x_p(1 - e^{-\tau^3}), \quad \tau = \left[\frac{(k_3 + k_5)A}{3}\right]^{1/3} t. \qquad \text{(IV)}$$

Fig.6 shows that in such a reaction the oxidised form of the catalyst accumulates at an increasing rate (auto-acceleration) until its concentration reaches a constant value and then remains unchanged.

Experimentally, quite a different picture is found (Figs.2 and 3). The rapid reduction of the oxidised form of the catalyst in the course of the oxidation may be due to accumulation of easily oxidised oxidation products which are produced after the hydroperoxide. Let us make one change

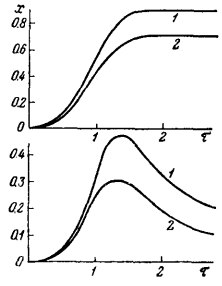


Fig. 6. Theoretical kinetic curves for the accumulation of the oxidised form of the catalyst in an oxidation reaction. Upper figure - M^{2+} and M^{3+} react only with the hydroperoxide [formula (IV): 1) $b = 0.9$; 2) $b = 0.7$]. Lower figure - M^{3+} is reduced by products formed from the hydroperoxide [formula (V): 1) $a = 0.5$; 2) $a = 1$].

in the above scheme, replacing the reaction M^{3+} with ROOH by the reaction

$$(M^{3+} + K \rightarrow M^{2+} + \text{radical } [3^1]),$$

where K is a product of the chain conversion of the hydroperoxide, formed at a rate $k[ROOH]n$:

$$\frac{d[K]}{dt} = k[ROOH]\sqrt{k_3[M^{2+}]_0[ROOH]/k^6};$$
$$[K] = B\,t^4; \quad B = {}^1/_3 A^{3/2} k \sqrt{k_3[M^{2+}]_0/k_6}.$$

The oxidised form of the catalyst will then accumulate at the rate:

$$\frac{d[M^{3+}]}{dt} = k_3[M^{2+}][ROOH] - k_4[M^{3+}][K]$$

or in dimensionless variables

$$\frac{dx}{d\tau} = (1-x)\tau^2 - ax\tau^4, \qquad (V)$$

where

$$x = \frac{[M^{3+}]}{[M^{2+}]_0}, \quad \tau = (k_3A)^{1/3}t, \quad a = k_4B(k_3A)^{-5/3}.$$

Fig.6 (lower curve) shows the change of x during the reaction, calculated with this formula; it is seen that this mechanism gives a good explanation of the experimentally observed kinetic curves for the accumulation of the oxidised form of the catalyst. Oxidation-reduction reactions between the catalyst and hydrocarbon oxidation products, such as alcohols, ketones, and aldehydes, are quite probable. It is known, for instance, that in aqueous acid solutions Co^{3+} rapidly oxidises formaldehyde and methyl and ethyl alcohols[41,42]. Analogous reactions apparently take place in solution in a hydrocarbon much more slowly, but at 100°–150° they may proceed fairly rapidly. These facts show convincingly that the reaction of cobalt(III) with aldehydes and other easily oxidised products of the incomplete oxidation has undoubted advantages over the reaction between Co^{3+} and ROOH→. It is appropriate here to recall that in the oxidation of aldehydes in acetic acid solutions the reaction of Co^{3+} with RCHO→ is much more rapid than the reaction between Co^{3+} and RCOOOH→.

In studying the catalysed oxidation of cyclohexane[21], it was noted that the rapid reduction of cobalt(III) coincides with the appearance of aldehydes in the cyclohexane. It is apparently these aldehydes which reduce the cobalt(III) during the oxidation reaction. Since the hydrocarbon undergoing oxidation contains hydroperoxides and aldehydes, the catalyst is continually being converted from one oxidation state to the other and back. Each transition is accompanied by the formation of a free radical, which starts a chain of conversions:

$$ROOH + St_2Co \rightarrow RO\cdot + St_2CoOH,$$
$$St_2CoOH + R_1CHO \rightarrow St_2Co + H_2O + R_1\dot{C}O.$$

Alcohols and ketones may react with the oxidised form of the catalyst similarly to aldehydes. Since the composition of the oxidation products changes continuously during the oxidation reaction, there is a continuous change in the relative amounts of oxidised and reduced forms of the catalyst. At the start of the reaction, only a hydroperoxide is formed, so that the concentration of the oxidised form increases. With the appearance of products possessing reducing properties (aldehydes, alcohols, etc.), the oxidised form of the catalyst is rapidly reduced, and its concentration diminishes.

The reaction of the catalyst with the oxidation products, with the formation of free radicals, may be considered as a degenerate branching of the chains which is accelerated by the catalyst. Of great interest, therefore, is the possibility of the initiation of chains by the catalyst in the initial system, containing only the hydrocarbon, dissolved oxygen, and the catalyst. If the catalyst is added to the hydrocarbon in a higher oxidation state, it can apparently form free radicals by the reaction

$$St_3Co + RH \rightarrow St_2Co + StH + R\cdot.$$

Free radicals are in fact formed by this type of reaction in the oxidation of trimethylethylene in acetic acid solution[43]. The study of the reactions of cobalt(III) with olefines has shown that the reaction of Co^{3+} with RH is rapid in aqueous acid solutions at room temperature[44]. The energy of activation of such a reaction is 27–29 kcal/mole, with a pre-exponential factor of 10^{20} litres $mole^{-1}$ sec^{-1}. At room temperature, k (Co^{3+}, olefine) varies from 0.3 to 6 litres $mole^{-1}$ sec^{-1}, depending on the hydrocarbon. Such reactions must proceed more slowly in solution in a hydrocarbon, where the catalyst is undissociated, but possibly occur at a rate sufficient to provide a reliable source of free radicals. In later stages of the oxidation such reactions do not apparently play a decisive part, reactions of the catalyst with the oxidation products predominating.

Catalysts such as cobalt and manganese salts are usually added to the hydrocarbon in the oxidation state(II). The question arises: do they participate in chain initiation at the start of the reaction, or does their initiating activity appear only with the appearance of a hydroperoxide? The possibility has been suggested[11,45] of chain initiation by reaction between cobalt(II) and oxygen under certain conditions:

$$St_2Co + O_2 \rightleftarrows St_2Co \ldots O_2,$$
$$St_2Co \ldots O_2 + RH \rightarrow St_2CoOOH + R\cdot$$
$$\text{or } St_2Co \ldots O_2 + RH \rightarrow St_2CoOH + RO\cdot.$$

Results supporting this mechanism were obtained in the oxidation of linoleic acid in benzene in the presence of cobalt stearate[45]. The rate of this reaction is independent of the concentration of hydroperoxide and is given by $\frac{d[ROOH]}{dt} = k[RH][St_2Co]$. Changing the polarity of the medium by adding nitrobenzene strongly affects the rate of the reaction (Table 2). Uri suggested that the catalyst forms a complex with oxygen which then reacts with another molecule of catalyst to form free radicals. A polar solvent (nitrobenzene) solvates the cobalt cations and hinders the formation of the complex with oxygen, and consequently, the formation of free radicals:

$$St_2Co + O_2 \rightleftarrows St_2Co \ldots O_2,$$
$$St_2Co \ldots O_2 + St_2Co(HX) \rightarrow St_2Co + St_2CoX + HO_2$$

The activity of a catalyst of variable oxidation state depends primarily upon the cation. To a first approximation, the higher the redox potential of its cation, the more active is the catalyst (Table 3)[46]. Table 3 shows that there is only a qualitative relationship between the maximum rate of oxidation and the redox potential. The relative activities of the catalysts change on passing from one oxidation process to another. This is quite understandable, since the ability of a catalyst to initiate a chain depends not only on its cation, but also on the composition of the reaction products, their activity in reactions with the catalyst, and the state of the catalyst in the reaction. In most cases the most active

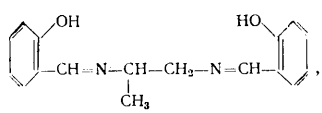
TABLE 2. Effect of the polarity of the solvent on the rate of oxidation of methyl linoleate (0.2 M) with 1.87×10^{-4} mole of St_2Co per litre.

Nitrobenzene, vol.%	Molar ratio of benzene to nitrobenzene	Rate of oxidation, mmoles $\times l^{-1} \times$ mole^{-1} h
0	—	14.4
25	3.74	13.4
30	2.70	12.3
35	2.14	7.6
40	1.74	3.88
45	1.42	1.86
50	1.16	0.68
75	0.385	0.0
100	—	0.0

catalysts are the salts of cobalt and manganese.

The lower the temperature, the more pronounced is the effect of the catalyst on the oxidation. At a low temperature the catalysed oxidation is much more rapid than the uncatalysed; as the temperature is raised, the difference in these rates decreases, because at a sufficiently high temperature the chain oxidation process can develop rapidly independently: the salt catalyst rapidly precipitates because of the accumulation of acids, and almost ceases to participate in the reaction.

The addition to the hydrocarbon of compounds which form complexes with metals of variable oxidation state affects their activity[47] because of the blocking action of the complex-forming agent, and possibly, because of a change in its redox potential. These complexing agents are used in practice; for example, very slight traces of copper in petrol (0.01 p.p.m.) decrease its stability. Disalicylidene-1,2-diaminopropane,



which forms chelate complexes with copper and deactivates it, is added to the petrol as a stabiliser[48,49].

The data on the catalysed oxidation of organic compounds leads to the following conclusion. In oxidation reactions catalysts of variable oxidation state play an active part in the initiation of chains. They react with the oxidation products (hydroperoxides, aldehydes, etc.), and in so doing change their oxidation state and produce free radicals. Each catalyst molecule can participate many times in the initiation of chains, converting the molecular oxidation products into free radicals. In this respect such catalysts differ substantially from initiators of the peroxide and azo-compound types. It must be emphasised that the detailed mechanism of the initiation of chains by catalysts has been insufficiently studied. Wide, strictly quantitative investigations of the individual elementary reactions in which various catalysts take part, are required.

TABLE 3. Effect of the redox potential of the catalyst on the maximum rate of oxidation of 2.5-dimethylhexane (61.4 mmoles) with 0.11 mmole of the stearates of various metals.

Catalyst cation	Max. rate of oxidation, mmoles of O_2 per hour per 61.4 mmoles of RH	Redox potential of cation (eV)
Co^{2+}	35	1.82
Mn^{2+}	32	1.51
Ce^{4+}	20	1.55
Fe^{3+}	13	0.77
Cd^{2+}	4	—

BREAKING OF CHAINS BY CATALYSTS OF VARIABLE OXIDATION STATE

The initiation of chains with participation of a catalyst takes place as a result of reactions of one or more "saturated-valency" molecules with a cation of variable oxidation state, in which the oxidation state of the catalyst changes and free radicals are formed. In principle the reverse reactions are also possible, reactions of free radicals with cations of variable oxidation state, leading to loss of the free valency. Since peroxide radicals are strong oxidising agents, they would be expected to react with the reduced form of the catalyst, e.g. by the reaction

$$RO_2\cdot + St_2Co \rightarrow ROO{-}CoSt_2 \text{ (or } St_2CoOH + \text{ketone)}.$$

In such a reaction, the peroxide radical forms a coordinate link, $RO_2{-}CoSt_2$, with the cation of variable oxidation state, using an unpaired electron of the cobalt(II). Reversible reactions of such ions are well known in aqueous solution, for example[50,51],

$$Fe^{3+} + OH^- \rightleftarrows Fe^{2+} + \cdot OH \text{ and } Fe^{3+} + H_2O_2 \rightleftarrows Fe^{2+} + HO_2\cdot + H^+$$

Thus, the ability of such cations to donate or accept an electron in reactions with molecules leads to the formation of free radicals, and in their reactions with free radicals, to the loss of these, with the formation of molecular products. In oxidation reactions such a catalyst initiates chains by reacting with molecular products, and breaks them by reacting with free radicals. The initiating action of the catalyst is usually much the stronger, and masks its inhibitory effect. The breaking of chains on variable-oxidation-state catalysts has been detected where the initiating action of the catalyst ceased to be effective after a time, and the catalyst (cobaltous or manganous stearate) showed only its inhibiting action[11,21]. The experiments were carried out as follows. The catalyst was added to cyclohexane, heated to 100°–110°, and the concentration of oxidation products and cobalt(III) was determined by sensitive analytical methods in samples of the oxidised cyclohexane taken during the course of the oxidation. When the catalyst had a high cobalt(III) content, the oxidation began immediately, at a constant and fairly high rate (Fig.7).

The situation is different if cobaltous stearate is added to the cyclohexane in concentrations of 0.01–0.05 mole %; a small part of the cobalt is converted to the +3-state, but most remains in the +2-state; for a time the oxidation is inhibited. This inhibition ceases when the cobalt has been converted to the +3-state and a hydroperoxide appears (Fig.8). The more cobalt(II) is added, the longer is the period of inhibition. This indicates a deceleration of the reaction by cobalt(II). An even clearer inhibiting action of

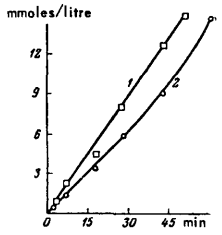


Fig. 7. Kinetic curves for the formation of 1) cyclohexanol and 2) cyclohexanone in the oxidation of cyclohexane in the presence of cobalt stearate containing 40% Co^{3+} (110°, $[Co^{3+}] + [Co^{2+}] = 0.07\%$).

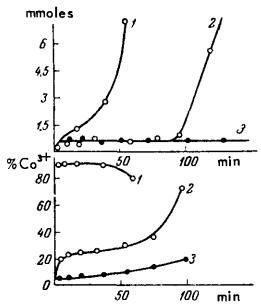


Fig. 8. Kinetics of the formation of cyclohexanone (upper figure) and of the change in the valency state of the catalyst (lower figure) in experiments on the oxidation of cyclohexane at 110° and 30 atm with various concentrations of St_2Co catalyst: 1) 0.003 mole%; 2) 0.02 mole%; 3) 0.07 mole%.

initiator of chains; it therefore behaves only as an inhibitor, reacting with free radicals and breaking the chains. An analogous effect is found in catalysis with manganese(II): at the start of low-temperature oxidation it functions as an oxidation inhibitor. From the very commencement of the reaction, cobalt(III) and manganese(III) act as chain initiators. The comparatively smooth converstion of cobalt(II) to cobalt(III) therefore causes a sudden change in the reaction, from inhibited to strongly catalysed.

Considering this in more detail, we shall attempt to construct the kinetic curves for the accumulation of the oxidised form of the catalyst and the oxidation products P, using a simple reaction scheme.

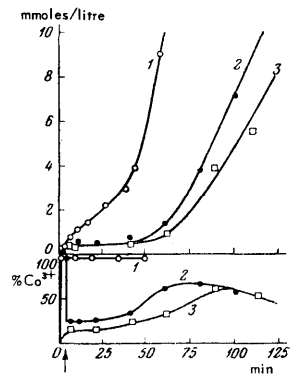


Fig. 9. Experiments on the oxidation of cyclohexane at 110° and 30 atm: 1) 0.003 mole% of St_2Co added initially; 2) 0.003 mole% of St_2Co added initially and a further 0.016 mole% in the fourth minute; 3) 0.018 mole% of St_2Co added initially. Upper figure - kinetics of the formation of the ketone; lower figure - kinetics of the formation of Co^{3+} in % of total Co concentration.

cobalt(II) on the oxidation of cyclohexane is observed when further catalyst is added to the reaction. A small quantity (0.003 mole %) of cobalt(II) added to the cyclohexane is completely converted to the +3-state, and the reaction starts immediately, without any inhibition (Fig.9, curve *1*). If to this reaction, once started, a further quantity of cobalt(II) is added, oxidation ceases for a time (Fig.9, curve *2*); the inhibition itself ceases with the conversion of a considerable part of the cobalt to the +3-state. An analogous effect is observed when a considerable quantity of cobalt(II) is needed in the reaction (Fig.9, curve *3*).

These facts are apparently contradictory — the more catalyst added to the hydrocarbon, the greater the inhibition of the oxidation — although it is known that cobalt(II) can initiate chains by reaction with a hydroperoxide. The behaviour of the catalyst in these experiments is explained in this way: at the start of the reaction, no hydroperoxide has yet been formed, and the cobalt(II) cannot act as an

Assume that in the chain-oxidation reaction, proceeding at a rate $k_2[RH]n$, the free radicals are formed mainly by the action of the oxidised form of the catalyst M^{3+} at a rate $k_4[RH][M^{3+}]$, and that the chains are broken with the participation of the reduced form of the catalyst at a rate $k_7[M^{2+}]n$, and without the participation of the catalyst at a rate $k_6'n$. Linear, and not quadratic, chain termination is assumed here for simplicity of calculation. At a stationary free radical concentration,

$$k_4[RH][M^{3+}] = (k_6' + k_7[M^{2+}])n\,,$$

$$\frac{d[P]}{dt} = k_2[RH]n = \frac{k_2 k_4 [RH]^2 [M^{3+}]}{k_6' + k_7[M^{2+}]}, \quad \text{or} \quad \frac{dy}{d\tau} = \frac{x}{a + 1 - x}, \qquad \text{(VI)}$$

$$y = y_0 + \int_{x_0}^{x} \frac{z\,d\tau}{a + 1 - z},$$

where x is the fraction of catalyst in the higher oxidation state:

$$x = \frac{[M^{3+}]}{[M^{2+}] + [M^{3+}]}, \quad a = \frac{k_6'}{k_7([M^{2+}] + [M^{3+}])}, \quad \tau = k_4[RH]\,t, \quad y = \frac{k_7[P]}{k_2[RH]}.$$

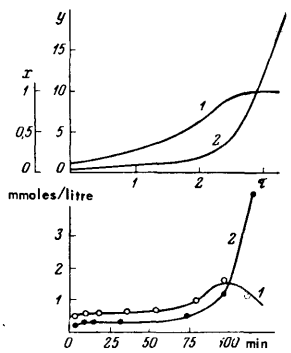


Fig. 10. Kinetic curves for the accumulation of 1) M^{3+} and 2) the oxidation product P in the initial period of the oxidation, with chain breaking by M^{2+} and chain initiation by M^{3+}. Upper figure - theoretical curves constructed from formulae (VI) and (VII) ($x_0 = 0.1$, $a = 0.05$, $y_0 = 0.05$). Lower figure - experimental data on the oxidation of cyclohexane at 110°, 30 atm, and St_2Co concentration 0.02 mole%: 1) Co^{3+}; 2) cyclohexanone.

Assuming that M^{3+} is formed only by reaction of M^{2+} with a free radical, we obtain

$$\frac{d[M^{3+}]}{dt} = \frac{k_4 k_7 [RH][M^{2+}][M^{3+}]}{k_6' + k_7[M^{2+}]} \quad \text{or} \quad \frac{dx}{d\tau} = \frac{x(1-x)}{a+1-x},$$
$$\ln \frac{x}{x_0} + a \ln \frac{1-x_0}{1-x} = \tau . \qquad \text{(VII)}$$

The change of x and y is shown in Fig.10, where they are compared with the kinetic curves for the accumulation of cobalt(III) and cyclohexanone in the oxidation of cyclohexane. The good agreement between calculation and experiment once more confirms the correctness of the suggested inhibitory action of cobalt(II) at the start of the reaction. The maximum in the experimental curve for the accumulation of cobalt(III) is associated with the appearance of aldehydes, which reduce the metal to the +2-state. The appearance in the reaction of a hydroperoxide converts even cobalt(II) from an inhibitor to a chain initiator.

The inhibiting action of cobalt(II) and manganese(II) is also shown by a number of other facts, which have not been correctly interpreted. Prolonged induction periods have been observed by Wibaut and Strong[22] in the oxidation of paraffinic hydrocarbons with cobaltous stearate; for example, in the oxidation of n-octane at 125°, in the presence of 1% cobalt stearate, the induction period is 10 h. The end of the induction period coincides with the rapid conversion of cobalt(II) to the +3-state. The addition of a hydroperoxide eliminates the induction period. In the oxidation of α-pinene[23] there is also a long induction period (8 h), but if cobaltic stearate is used instead of the cobaltous salt, the oxidation commences immediately, as is the case if cobalt(II) is added to α-pinene containing a hydroperoxide. The use of manganous stearate causes an induction period in the oxidation of Synthin[24]; the induction period is longer the more manganese stearate is used.

These facts are explained simply if breaking of the chains by the +2-state of the catalyst is taken into account. At the start of the reaction, the cobalt(II) [or manganese(II)] only breaks the chains, and so creates a long induction period. The addition of cobalt(III), which does not react with peroxide radicals but initiates chains, only accelerates the reaction, and there is no induction period. A hyderoperoxide added to the system, hydrocarbon — oxygen — catalyst reacts with cobalt(II) to form free radicals and thus eliminates the induction period.

In the later stages of the reaction the initiation of chains by the reaction of the reduced form of the catalyst with the hydroperoxide predominates over the breaking of chains by the catalyst molecules. Moreover, in the later stages of the oxidation the free radical concentration n is much greater than at the start of the process. Under these conditions the rate of quadratic chain termination, $k_6 n^2$, is much greater than the rate of linear chain termination by the catalyst, $k_7[M^{2+}]n$. Hence, in the later stages of the reaction the inhibitory action of the catalyst hardly appears. It can be detected by measuring the order of the reaction relative to the catalyst. With quadratic termination of chains and their initiation with the participation of one molecule of catalyst, $v \propto n \propto [\text{catalyst}]^{1/2}$. If the catalyst also participates in the breaking of chains, the order of the reaction relative to the catalyst concentration must be less than 0.5. In the oxidation of cyclohexene in the presence of the stearates of cobalt(II), copper(II), and manganese(II),[38] it was found that the order of the reaction relative to the manganese stearate concentration was 0.36, and relative to the copper stearate concentration, 0.40; with manganese stearate the induction periods are long. The inhibiting action of copper(II) on the oxidation of n-decane is significant[27]. In this reaction copper stearate produces an induction period which depends in a very singular fashion on the concentration of added catalyst. Up to a copper concentration of 0.6 mole % the induction period increases smoothly with concentration, but a further slight increase in its concentration causes a much increased induction period (Fig.11). The presence of a critical copper stearate concentration of 0.6 mole % in the oxidation of decane is connected with the double function of this catalyst and the

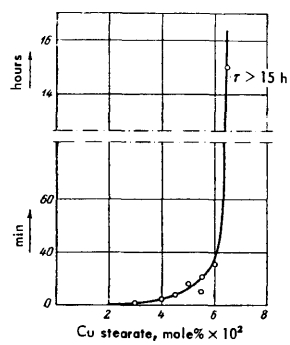


Fig. 11. Effect of the concentration of added copper stearate on the induction period in the oxidation of n-decane at 140°.

degenerate-branching chain mechanism of the reaction. The inhibiting action of copper stearate on oxidation reactions has been observed in the case of the oxidation of octenes[52] and paraffins[52]. On the other hand, the oxidation of ethylbenzene[52], cyclohexane[21], and lubricating oil[20] is accelerated by a copper catalyst. The inhibitory effect of copper(II) is usually found when it is present in fairly high concentration; traces of copper, as a rule, accelerate oxidation.

Catalysts of variable oxidation state (salts of cobalt, manganese, and copper) can thus not only initiate chains, but can break them also. Depending on the conditions, one of these functions predominates, so that the catalyst can act as an initiator or as an inhibitor. The detailed quantitative investigation of the inhibitory function of the catalyst merits very serious attention. It is important to compare the effectiveness of inhibition by different cations of variable oxidation state, to investigate how this effect varies with the medium (solvent), the nature of the anion of the catalyst, and the structure of the peroxide radicals, to determine the velocity constants of the elementary reactions of peroxide radicals with the catalyst, and so on. Investigations of this type are only just beginning, and data on all these questions are not available.

PHYSICOCHEMICAL PROPERTIES OF SOLUTIONS OF SALT CATALYSTS IN HYDROCARBONS

In addition to the chemical properties of catalysts, their physicochemical state in the hydrocarbon solution has a substantial influence. Knowledge of solutions of metal salts of organic acids in hydrocarbons provides a correct understanding of certain kinetic features of the catalysed oxidation of hydrocarbons and of the changes which the catalyst undergoes during the reaction as a result of the accumulation of various oxidation products. Catalysts of variable oxidation state are added to the hydrocarbon as salts of fatty or naphthenic acids; in a polar solvent the salts dissociate into ions, but in a hydrocarbon solvent dissociation does not occur. This is shown by conductivity measurements on hydrocarbon solutions of metal salts of fatty acids: the conductivity of benzene solutions of copper, nickel, and cobalt oleates is practically the same as that of pure benzene[53], and the conductivity of dilute toluene solutions of zinc, lead, copper, magnesium, and calcium oleates is little different from that of pure toluene[54]. As the salt concentration increases, the equivalent conductance also increases, because of the formation of micelles from the salt molecules, and their easier dissociation into ions[54].

Each molecule of carboxylic acid metal salt is a dipole, and the electrostatic attraction of these dipoles in the non-polar solvent causes the salt molecules to combine into micelles. The formation of micelles can be considered as a series of successive equilibria:

$$MA_2 + MA_2 \rightleftarrows (MA_2)_2,$$
$$MA_2 + (MA_2)_2 \rightleftarrows (MA_2)_3,$$
$$\cdots\cdots\cdots\cdots$$
$$MA_2 + (MA_2)_{n-1} \rightleftarrows (MA_2)_n.$$

Experimental proof of the association of salt molecules in the hydrocarbon solution is furnished by the higher molecular weight of the dissolved salt, determined ebullioscopically. For example, the molecular weight of copper stearate at a concentration of 0.02–0.08% in lubricating oil is 5000 instead of 347, and the molecular weight of iron stearate, at a concentration of 0.01–0.04%, is 1700 instead of 339.[20] The association of salts in toluene solutions has been studied in detail[55–57]. The degree of association increases with the salt concentration (Table 4), in good agreement with the existence of such equilibria.

TABLE 4. Micellar weights of various soaps in toluene*.

Zn laurate			Zn stearate			Cu stearate		
C	M	N	C	M	N	C	M	N
0.653	2310	4.98	0.938	3460	5.47	1.038	4040	6.43
1.335	2840	6.13	1.690	3400	5.38	1.647	4220	6.70
1.935	3040	6.56	2.650	3530	5.58	2.580	4470	7.10

* C = concn. of soap in g/100 g; M = micellar weight; N = number of slat molecules per micelle.

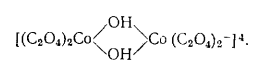
Since the combination of salt molecules into micelles occurs as a result of the electrostatic interaction between the dipoles of the molecules, the micellar weight must increase with the dipole moment, and this is found in practice (Table 5).

TABLE 5. Micellar weight of metal laurates as a function of dipole moment.

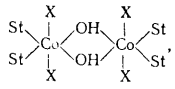
Metal	Micellar weight of laurate	Dipole moment of laurate
Zn	2600	0.29
Cu	3500	1.20
Mg	6000	1.66
Ni	20000	2.67

The degree of association depends on the length of the acid residue, and decreases as this length increases. The degree of association falls as the temperature is raised. To a first approximation, all these features of the behaviour of hydrocarbon solutions of salts of fatty acids can be explained by the electrostatic attraction of the polar molecules in the non-polar solvent. The mean interaction potential between two isolated dipoles $N = -2\mu_1^2\mu_2^2/3r^6kT$, where μ_1 and μ_2 are the dipole moments of the species, r is their radius, k the Boltzmann constant, and T the absolute temperature. It follows from this expression that the degree of association will be smaller the smaller the polarity of the cation of the salt, the larger the number of C atoms in the acid residue (the larger r), and the higher the temperature.

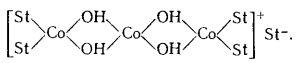
In some cases the association of catalyst molecules into larger particles takes place by the formation of polynuclear complexes, i.e. it is chemical in nature. For example, cobalt(III) tends to form polynuclear complexes of the type



The formation of the complex



where St is the stearic acid residue and X is water or alcohol, has been suggested in the catalysed oxidation of α-pinene[23]. Freidin[24] isolated the salt of cobalt(III) formed in the oxidation of Synthin and determined its empirical formula and molecular weight, concluding that the cobalt(III) is present in the hydrocarbon as the trinuclear complex:



The formation of salt molecules into micelles must be taken into account in considering the mechanism of the catalysed oxidation of hydrocarbons. The activity of the catalyst depends upon the degree of association of its molecules and the activity is proportional to a first approximation, to the number of catalyst particles in unit volume of the hydrocarbon being oxidised. The closer the approach of the catalyst solution to a true solution, the higher its activity, other conditions being equal. The influence of the acid residue on the catalyst activity is apparently due to this circumstance. The higher the molecular weight of the acid component of the salt, the more active is the catalyst[58,59]. Exceptions to this rule are apparently caused by the different methods of preparing the catalysts, which might contain water of crystallisation, might be partly present as a basic salt, and so on, which would affect the state of the catalyst in the hydrocarbon solution.

The combination of molecules of the salts into micelles is closely connected with the relation between the concentration of the catalyst and its effect on the reaction. If the catalyst forms a true solution in the hydrocarbon, the rate of initiation of chains by the catalyst should increase linearly with its concentration. The formation of micelles changes the picture: as the concentration of dissolved salt increases, the number of particles in unit volume first increases in proportion to the concentration, but then the increase slows down and practically levels off — further increase in the salt concentration causes an increase in the size of the micelles. Accordingly, the initiation of chains by the catalyst first increases as its concentration increases, and then this increase ceases. Fig.12 shows how the rate of chain initiation varies with the concentration of copper stearate in the oxidation of lubricating oil[20].

The rate of formation of free radicals determines the rate of oxidation, and so the same relation is observed between the maximum rate of the catalysed oxidation and the catalyst concentration[22,58,60-64]. Some workers consider this relation between the rate of oxidation and the catalyst concentration as proof that the catalyst takes part in the breaking of chains. Since the association of the catalyst molecules leads to an analogous picture and the effect of this association on the initiating capacity of the catalyst has been demonstrated experimentally[20], the above interpretation of the dependence of the rate of oxidation on the catalyst concentration is not necessarily valid. This is shown also by the fact that in acetic acid, where the catalyst forms a true solution, both the rate of chain initiation and the rate of oxidation increase linearly with the catalyst

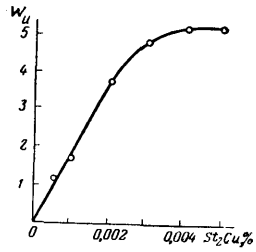


Fig. 12. Dependence of the rate of initiation w_u (in relative units) on the concentration of added copper stearate in the oxidation of liquid paraffin at 150°.

concentration[3,5,43]. It does not follow from this that variable-oxidation-state catalysts do not break chains in the advanced stages of the reaction; breaking of chains by the catalyst does apparently take place, but under these conditions the initiating function of the catalyst is much stronger than its inhibitory capacity. Moreover, with a high free-radical concentration in the later stages of the reaction, the rate of quadratic termination is high, and in comparison with this, the linear termination of chains by the catalyst molecules is insignificant. The inhibitory function of the catalyst is clearly shown, as we have seen, at the start of the reaction, when the catalyst does not initiate chains.

MACROSCOPIC STAGES IN THE CATALYTIC OXIDATION OF HYDROCARBONS

The vapour-phase oxidation of hydrocarbons in the presence of homogeneous catalysts takes place[65], as a succession of macroscopic stages separated in time[65]. The decisive part is played by the first macroscopic stage, the completion of which at the start of the process determines further development of the latter. Such separate stages were detected and studied in the oxidation of propane with hydrogen bromide as catalyst. It was shown that at the start, there is an initiating reaction which forms an intermediate product, and soon ceases. During the reaction this intermediate decomposes to form free radicals which initiate the second stage, the oxidation of propane to acetone. Later studies of the oxidation of propane, ethane, and methane in the presence of HBr, Cl_2, and NO_2, established that macroscopic stages in oxidation reactions with a homogeneous catalyst are widespread[65,66]. Macroscopic stages are also observed in the liquid-phase oxidation of hydrocarbons with catalysts of variable oxidation state. Tsyskovskii and Kiseleva[7,59] first drew attention to the fact that in the oxidation of kerosene with manganese naphthenate, the catalyst is in the dissolved state and initiates the reaction only at the start of the oxidation. The catalyst then precipitates completely and takes no further part in the oxidation. Knorre, et al.[8] studied the kinetics of the oxidation of n-decane in the presence of cobalt and manganese stearates, and showed that the catalyst first undergoes a change of oxidation state, and then precipitates and takes no noticeable part in the oxidation. Thus the catalysed oxi-

dation of hydrocarbons often takes place in two stages: in the first, the catalyst is in solution and accelerates the oxidation by initiating chains; in the second, it is in the precipitate, and takes no part in chain initiation. This sharp separation of the reaction into two stages is not always found: for instance, in the catalysed oxidation of cyclohexane the catalyst is not completely precipitated, so that its effect on the reaction decreases gradually during the course of the oxidation[10].

The presence of macroscopic stages in the catalysed oxidation of hydrocarbons is apparently caused by a change in the physicochemical stage of the catalyst in the hydrocarbon solution as the molecular oxidation products accumulate. In acetic acid, where the catalyst is always present as ions, macroscopic stages are not observed. In a hydrocarbon the catalyst is extremely sensitive to the presence of polar substances; its solubility depends greatly on the polarity of the medium and the anionic component of the salt. The formation of complexes with the oxidation products can affect its activity. Of the oxidation products which act upon the state of aggregation of the catalyst, the acids are important. It has often been found in experiments that the catalyst is precipitated in oxidation reactions as salts of acids formed by the oxidation. Thus in the oxidation of kerosene the catalyst precipitates as a salt of low-molecular weight acids formed in the reaction[59]; in the oxidation of cyclohexane, the cobalt, added as stearate, precipitates as the adipate[10]. However, the precipitation of the catalyst during the oxidation is not the result of a simple exchange reaction between the salt and the acid, but of a more complex physiocochemical process in which other reaction products, particularly water, take part as well as the acids.

Some workers have noted a decreased catalyst activity even when it is not precipitated. In the oxidation of cyclohexane in the presence of copper stearate the rate of oxidation falls rapidly in the course of the reaction; with the introduction of fresh catalyst, the reaction again proceeds rapidly, and then slows down[21] (Fig.13). Possibly, the catalyst loses its activity by undergoing a change in the chain initiation process itself, for example by reaction with a hydroperoxide. The activity of copper stearate also decreases rapidly in the catalysed decomposition of ethylbenzene hydroperoxide[39].

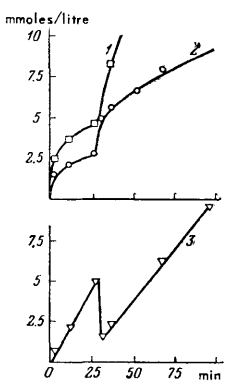


Fig. 13. Oxidation of cyclohexane at 110° with the introduction of St_2Cu (0.75 mmole/litre) initially, and 1.0 mmole/litre in the 60th minute: [30th minute? (Ed. of Translation)] 1) cyclohexanol; 2) cyclohexanone; 3) cyclohexyl hydroperoxide.

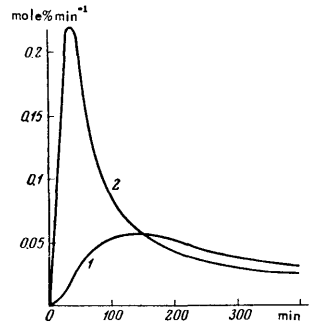


Fig. 14. Change of the rate of oxidation of n-decane at 140° in the course of the oxidation; 1) without catalyst; 2) with 0.3 mole% St_2Co.

The presence of an initial macroscopic stage is shown in the oxidation kinetics by the initial rapid increase in the rate of oxidation, which reaches a maximum and then rapidly falls (Fig.14). The decreased rate in later stages of the reaction is due to precipitation of the catalyst. At the commencement of the reaction the catalyst takes an active part in the initiation of chains, and, as hydroperoxides and other oxidation products accumulate, the rate of chain initiation by the catalyst grows. The appearance of products which cause precipitation of the catalyst or reduce its activity because of the formation of complexes, decreases the role of the catalyst in the initiation of chains. This naturally affects the rate of oxidation. The reason for the catalysed oxidation occurring in stages can be explained only in very general terms. Further and more detailed study of these phenomena is necessary, in particular, the development of methods for preventing the deactivation of the catalysts in the course of the oxidation.

CONTROLLING FUNCTION OF THE CATALYST IN OXIDATION REACTIONS

The role of the catalyst in an oxidation reaction is confined, in many cases, to its participation in the initiation and breaking of chains. Often, however, the catalysts affect not only the rate, but also the composition of the products of the oxidation, i.e. they have a controlling function. The direct influence of the catalyst on the composition of the oxidation products is seen in the catalysed oxidation of cyclohexane. The main intermediate oxidation products in the oxidation of cyclohexane are cyclohexanone and cyclohexanol. In the absence of catalyst the ketone forms in about twice the quantity of the alcohol; in the presence of cobalt stearate the amount of the alcohol is about 1.5 times that of the ketone[10,11].

The controlling action of the catalyst is not connected with its initiating capacity, as is shown by comparing the oxidation of cyclohexane in the presence of cobalt stearate and cobalt adipate (Fig.15). The latter is poorly soluble in cyclohexane and does not accelerate the oxidation, but both

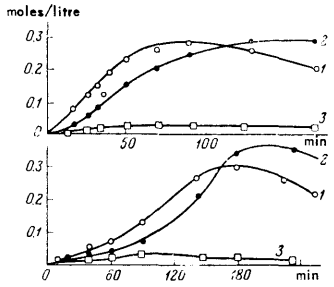


Fig. 15. Kinetic curves for the accumulation of 1) cyclohexanol, 2) cyclohexanone, and 3) cyclohexyl hydroperoxide in the oxidation of cyclohexane in the presence of 0.06 mole% St_2Co (upper figure) and 0.055 mole% of cobalt adipate (lower figure).

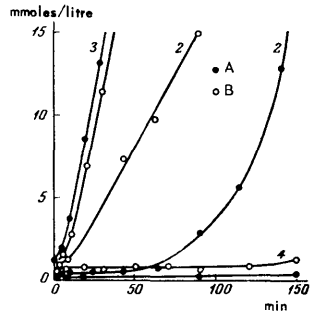


Fig. 16. Kinetic curves for the accumulation of cyclohexanone (A) and cyclohexanol (B) at the commencement of the oxidation of cyclohexane in the presence of 0.017 mole% St_2Co at: 1) 100°; 2) 110°; 3) 121°.

catalysts provide the alcohol : ketone ratio characteristic of the catalysed oxidation. If the catalyst is removed from the cyclohexane, this ratio rapidly changes and becomes that for the uncatalysed reaction.

The controlling action of the catalyst has been observed in the oxidation of paraffin with a manganese catalyst[67].

In the catalysed oxidation of cyclohexane the alcohol and ketone are formed and react by a chain mechanism[21]. The relative proportions of the products are completely determined by the chain-propagation reactions and are independent of the initiation and breaking of chains. This proportion can only be altered by acting upon the chain-propagation reactions; consequently, the influence of the catalyst on the composition of the products of the chain reaction must be the result of its participation in the chain-propagation reaction. In this connection, the following feature of the reaction is interesting. The addition of cobaltous stearate to cyclohexane at 100° slows down the formation of the ketone and the alcohol; at 120° the catalyst is immediately converted into the +3-state and both products simultaneously accumulate in the reaction. At 110° the catalyst is only partially converted into the +3-form, and the remaining cobalt(II) slows down the formation of the ketone, but not of the alcohol[11] (Fig.16). Analogous effects are found in the oxidation of cyclohexane with manganese stearate, where the alcohol begins to form much earlier than the ketone (Fig.17).[21] This indicates that in the presence of a catalyst, the alcohol and ketone are formed by two parallel independent routes. In the uncatalysed oxidation, they are formed according to the scheme[68,69]

$$\text{hydrocarbon} \rightarrow RO_2 \rightarrow \text{hydroperoxide} \begin{cases} \nearrow \text{alcohol} \\ \searrow \text{ketone} \end{cases} \rightarrow \text{acids}.$$

The catalyst apparently changes the routes of formation of these products, since this scheme cannot explain why the catalyst slows down the formation of the ketone, but not of the alcohol.

Experiments on the oxidation of cyclohexane with iron and nickel stearates have shown that at the start of the reaction there is parallel formation of the hydroperoxide, alcohol, and ketone[12] (Fig.18). This indicates the conversion of part of the peroxide radicals, in the presence of the catalyst, into the alcohol and ketone, without passing through

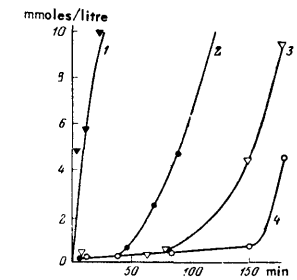


Fig. 17. Kinetic curves for the formation of 1) the alcohol and 2) the ketone in the oxidation of cyclohexane in the presence of 0.004 mole% St_2Mn, and similarly 3) and 4) in the presence of 0.017 mole% St_2Mn, at 110°.

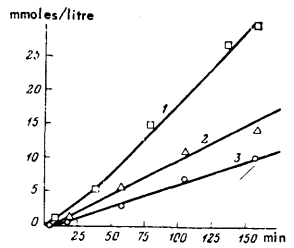


Fig. 18. Kinetic curves for the formation of 1) cyclohexanol, 2) cyclohexyl hydroperoxide, and 3) cyclohexanone at the commencement of oxidation of cyclohexane at 110° in the presence of 0.018 mole% St_3Fe.

the stage of hydroperoxide formation, i.e. it indicates that the catalyst participates in the chain-propagation reaction. To substantiate this conclusion, consider the two mechanisms for the chain oxidation of the hydrocarbon. Consider first the oxidation through hydroperoxide formation. Let the hydrocarbon be completely converted in the oxidation to hydroperoxide, at a rate $k_2[RH]n$, and let the hydroperoxide

be converted by a chain mechanism to product P at a rate $k_4[ROOH]n$. If the chains are initiated at a constant rate w_0, then with quadratic chain termination $n = \sqrt{w_0/2k_6}$, and the rates of accumulation of ROOH and P are

$$\frac{d[ROOH]}{dt} = (k_2[RH] - k_4[ROOH])\sqrt{\frac{w_0}{2k_6}},$$

$$\frac{d[P]}{dt} = k_4[ROOH]\sqrt{\frac{w_0}{2k_6}}.$$

On introduction of the notation

$$\pi = \frac{[ROOH]}{[ROOH]_{max}}, \quad [ROOH]_{max} = \frac{k_2[RH]}{k_4},$$

$$\tau = k_4\sqrt{\frac{w_0}{2k_6}}[ROOH]_{max}\, t, \quad \eta = \frac{[P]}{[ROOH]_{max}},$$

the equations take the form

$$\frac{d\pi}{d\tau} = 1 - \pi, \quad \frac{d\eta}{d\tau} = \pi.$$

hence $\pi = 1 - e^{-\tau}$, $\eta = \tau + e^{-\tau} - 1$.

At the start of the reaction $\frac{d\pi}{d\tau} = 1$ and $\frac{d\eta}{d\tau} = 0$.

The change of π and η with time is shown in Fig.19, where it is seen that at the start of the reaction π (curve *1*) increases linearly, and η autocatalytically (curve *2*).

Consider now the second mechanism, assuming part of the peroxide radicals to be converted by reaction with the catalyst M into product P and radical X, which can continue the chain. To a first approximation, it can be assumed, as before, that all the radicals combine quadratically at a rate $2k_6n^2$. Here the product P will form as a result of two reactions:

$$ROOH + RO_2\cdot\,(\text{or } X\cdot), \text{ and } RO_2\cdot + M \qquad (7)$$

at a rate

$$\frac{d[P]}{dt} = k_4[ROOH]n + k_7[M][RO_2\cdot]$$

or in dimensionless variables

$$\frac{d\eta}{d\tau} = a + \pi,$$

where

$$a = \frac{k_2'k_7[M][RH]}{k_4[ROOH]_{max}(k_7[M] + k_2'[RH])},$$

k_2' relates to the reaction $X\cdot + RH \rightarrow$

$$\eta = (a+1)\tau + e^{-\tau} - 1.$$

At sufficiently high values of a the kinetic curves for η are in this case similar to those of π (Fig.19). Comparison of Figs.18 and 19 shows the good agreement between the calculated and the experimental data. A similar situation is observed in experiments on the oxidation of cyclohexane in the presence of nickel and cadmium stearates (Table 6).

The participation of the catalyst in the chain-propagation reaction can be considered either as a reaction between a radical and the catalyst, forming a molecular product and a new radical, or as the formation of a complex between the catalyst and a free radical, the complex being active in the chain propagation reaction. Recent studies[70-72] indicate the formation of complexes between free radicals or atoms and molecules, for instance aromatic hydrocarbons. Similar

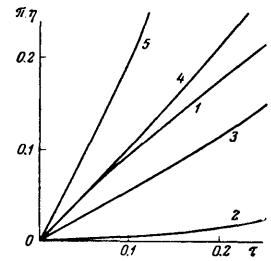


Fig. 19. Curves of π and η as functions of τ calculated from the formulae: 1) $\pi = 1 - e^{-\tau}$; 2) $\eta = \tau + e^{-\tau} - 1$; 3) $\eta = 3/2\,\tau + e^{-\tau} - 1$; 4) $\eta = 2\tau + e^{-\tau} - 1$; 5) $\eta = 3\tau + e^{-\tau} - 1$.

TABLE 6. Initial rates of accumulation of peroxide, alcohol, and ketone in the oxidation of cyclohexane at 110° ($v = v_{ROOH} + v_{alcohol} + v_{ketone}$)

Catalyst	Concn.	$\frac{v_{ROOH}}{v}\times 100\%$	$\frac{v_{alcohol}}{v}\times 100\%$	$\frac{v_{ketone}}{v}\times 100\%$
St_2Fe	0.018	29	55	16
St_2Ni	0.024	32	34	34
St_2Cd	0.011	55	28	17

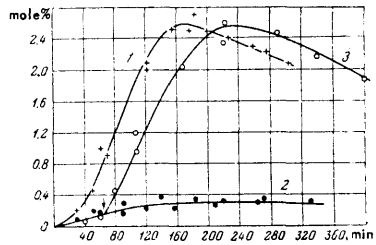


Fig. 20. Kinetics of the accumulation of hydroperoxide in the oxidation of n-decane at 140°: 1) without a catalyst; 2) with 0.3 mole% St_2Co; 3) with removal of the catalyst from the reaction zone (time of removal arrowed).

complexes may be formed between peroxide radicals and cations of metal salts; such complexes might gradually decompose or react with the hydrocarbon to form the alcohol or ketone. If the catalysts participate in the chain propagation reaction as suggested, the catalysts must influence the rate of chain propagation; in principle, this can be established by the intermittent-illumination method[73].

The suggested participation of the catalyst in chain propagation can explain the effect of the catalyst concentration on the maximum concentration of hydroperoxide and the maximum rate of reaction. It has frequently been observed that as the catalyst concentration is increased, the maximum concentration of hydroperoxide decreases, while the maximum reaction velocity increases. The catalyst causes the diminished hydroperoxide concentration, since its removal from the reaction zone produces a rapid increase in hydroperoxide concentration[69] (Fig.20).

These two simple facts are incorrectly explained in a number of proposed mechanisms. The following mechanism for the oxidation, for instance, is widely quoted:

$$ROOH \rightarrow RO\cdot + \cdot OH, \quad (1)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot,\ RO_2 + RH \rightarrow ROOH + R\cdot, \quad (2)$$

$$ROOH + M \rightarrow M^+ + OH^- + RO\cdot, \quad (3)$$

$$2RO_2\cdot \rightarrow \text{mol. products}. \quad (6)$$

According to this mechanism, the maximum hydroperoxide concentration decreases with increased catalyst concentration:

$$\frac{d[ROOH]_{max}}{dt} = k_2[RH][RO_2\cdot] - (k_3[M]+k_1)[ROOH] = 0,$$

$$[RO_2\cdot] = \left[\frac{(k_1 + k_3[M])[ROOH]}{2k_6}\right]^{1/2},\ [ROOH]_{max} = \frac{k_2^2[RH]^2}{2k_6(k_3[M] + k_1)}.$$

However, the maximum rate of oxidation is independent of the catalyst concentration:

$$v_{max} = k_2[RH][RO_2\cdot] = \frac{k_2^2[RH]^2}{2k_6}.$$

When the maximum hydroperoxide concentration is reached, the process changes from a chain reaction to a radical reaction:

$$k_2[RH][RO_2\cdot] = (k_1 + k_3[M])[ROOH].$$

Such a mechanism is justified in some cases, e.g. in the oxidation of tetralin in acetic acid solution[17]. It does not, however, take into account the reaction between free radicals and the hydroperoxide, i.e. the chain decomposition of the hydroperoxide; let us consider therefore a mechanism which allows for this:

$$ROOH \rightarrow RO\cdot + \cdot OH, \quad (1)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot,\ RO_2\cdot + RH \rightarrow ROOH + R\cdot, \quad (2)$$

$$ROOH + M \rightarrow M^+ + OH^- + RO\cdot, \quad (3)$$

$$ROOH + RO_2\cdot \rightarrow P + R'\cdot, \quad (4)$$

$$2RO_2\cdot \rightarrow \text{mol. products}. \quad (6)$$

If the chain decomposition of the hydroperoxide predominates, then

$$\frac{d[ROOH]_{max}}{dt} = (k_2[RH] - k_4[ROOH])n = 0,\ [ROOH]_{max} = \frac{k_2}{k_4}[RH],$$

$$v_{max} = k_2[RH]n = k_2[RH]\left[\frac{k_2[RH](k_1 + k_3[M])}{2k_4k_6}\right]^{1/2}.$$

This mechanism explains the growth of v_{max} with increase of [M], but is inconsistent with the dependence of $[ROOH]_{max}$ on [M].

Good agreement between experiment and calculation is obtained if the catalyst is assumed to take part in the chain propagation by the reaction given above with the additional step

$$RO_2\cdot + M \rightarrow X\cdot + P. \quad (7)$$

Let us denote the velocity constant of the reaction between RH and X· by k_2' and assume that the rate of second-order chain breaking is independent of the type of chain. The concentrations of $RO_2\cdot$ and X· in the reaction are in kinetic equilibrium:

$$k_2'[RH][X\cdot] = k_7[M][RO_2\cdot]$$

hence we find:

$$[RO_2\cdot] = \frac{k_2'[RH]n}{k_2'[RH] + k_7[M]},\ n = [RO_2\cdot] + [X\cdot].$$

The rate of accumulation of hydroperoxide in this reaction is

$$\frac{d[ROOH]}{dt} = k_2[RH][RO_2\cdot] - k_4[ROOH]n = \left(\frac{k_2k_2'[RH]^2}{k_2'[RH] + k_7[M]} - k_4[ROOH]\right)n,$$

hence

$$[ROOH]_{max} = \frac{k_2k_2'[RH]^2}{k_4(k_7[M] + k_2'[RH])}$$

and decreases with increase of [M].

The maximum rate of oxidation at small values of [M] increases with catalyst concentration, but the reaction remains a chain one all the time:

$$v_{max} = (k_2[RO_2\cdot] + k_2'[X\cdot])[RH] = k_2'[RH]^2\frac{k_2[RH] + k_7[M]}{k_2'[RH] + k_7[M]} \times$$

$$\times \sqrt{\frac{(k_1 + k_3[M])k_2k_2'}{2k_4k_6(k_2'[RH] + k_7[M])}} =$$

$$= k_2^2[RH]^2\sqrt{\frac{k_3[M]}{2k_4k_6(k_2[RH] + k_7[M])}}\ (\text{when } k_2 = k_2' \text{ and } k_3[M] \gg k_1).$$

Another reaction mechanism is also possible to explain the decrease in $[ROOH]_{max}$ and the increase in v_{max} as the catalyst concentration is increased. Assume that the hydroperoxide decomposes under the action of the catalyst by two routes: (*i*) without the formation of free radicals, and (*ii*) with the formation of free radicals, all the peroxide radicals being converted into hydroperoxide:

$$ROOH \rightarrow RO\cdot + \cdot OH, \quad (1)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot\ RO_2 + RH \rightarrow ROOH + R\cdot, \quad (2)$$

$$ROOH + M \rightarrow PO\cdot + M + \cdot OH, \quad (3)$$

$$ROOH + M \rightarrow \text{mol. products}, \quad (5)$$

$$2RO_2 \rightarrow \text{mol. products}. \quad (6)$$

According to this mechanism,

$$[ROOH]_{max} = \frac{k_2^2[RH]^2(k_1 + k_3[M])}{2k_6[k_1 + (k_3 + k_5)[M]]^2} \simeq \frac{k_2^2k_3[RH]^2}{2k_6(k_3 + k_5)^2[M]},$$

$$v_{max} = \frac{k_2^2[RH]^2(k_1 + k_3[M])}{2k_6[k_1 + (k_3 + k_5)[M]]} \simeq \frac{k_2^2k_3[RH]^2}{2k_6(k_3 + k_5)}.$$

All the data obtained up to the present indicate a complex and multiple action of salt catalysts in an oxidation reaction. The catalysts react with oxidation products such as hydroperoxides and aldehydes to form free radicals. Moreover, some catalysts react with the free radicals and so break the chains; under certain conditions, such catalysts act as oxidation inhibitors. Furthermore, salt catalysts participate in chain-propagation reactions, and affect the composition of the resulting oxidation products. The catalysts undergo complex physicochemical modifications in the course of the oxidation. The final products of the reaction, particularly acids, precipitate the catalyst, and the reaction then proceeds with only very slight participation of the catalyst.

It is extremely important, however, that in spite of the great complexity of the catalysed oxidation of hydrocarbons, there is already sufficient understanding of a number of the phenomena involved to enable various problems in the control of the oxidation process to be recognised and solved.

Further study will undoubtedly lead to the establishment of a detailed mechanism, and to the explanation of the many singular features of catalysis by salts of metals of variable oxidation state. These studies will enable precise methods of controlled oxidation to be achieved in practice, based on the knowledge of the elementary processes involved in the catalysed oxidation of hydrocarbons and other organic substances.

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METHODS OF SYNTHESIS OF POLYPHENYL HYDROCARBONS

M. S. Shvartsberg and I. L. Kotlyarevskii

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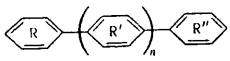
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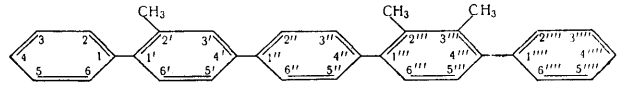
INTRODUCTION

The term polyphenyls is used for compounds whose molecules consist of a chain of substituted or unsubstituted phenyl and phenylene units.



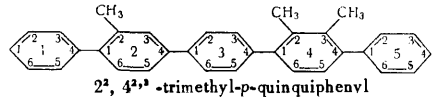
Each inner, phenylene, link of the molecule carries two aromatic residues in the *ortho*-, *meta*-, or *para*-position to one another; hence the existence of *ortho*-, *meta*-, and *para*-polyphenyls as well as mixed ones. The nomenclature is based on the use of latin numerical prefixes to give the number of aromatic nuclei in the molecule (e.g. terphenyl, quaterphenyl), the type of the polyphenyl also being indicated. The carbon atoms in each ring are numbered from the one linked to the preceding nucleus. In the "leading" phenyl radical the numbering starts either at the carbon linked to another nucleus or the one in the *para* -position to it. In the former case the rings are designated by primes, the position of the substituent being indicated by numerals. In the latter case the numeral denotes the ring containing the substituent and the numerical superscript the position of the substituent in the ring. Both methods are illustrated below:

1.



2′, 2″, 3‴-trimethyl-*p*-quinquiphenyl

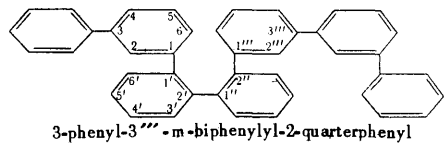
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$2^2, 4^{2,3}$-trimethyl-*p*-quinquiphenyl

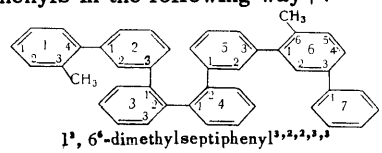
The second method is more convenient for compounds with a large number of rings[1].

Mixed polyphenyls are named by taking a part of the polycyclic chain with the same relative positions of the units and considering it as the main one, e.g.



3-phenyl-3‴-*m*-biphenylyl-2-quarterphenyl

We suggest an extension of the numeral method to mixed polyphenyls in the following way†:



$1^3, 6^6$-dimethylseptiphenyl$^{1^3,2^2,2^3,3^3}$,

the superscript numerals following the name indicating the points of attachment of subsequent rings, starting from the second one.

The interaction of non-condensed aromatic rings gives rise to a characteristic electronic structure of the polyphenyl chain and gives these compounds their specific properties which justify their classification as a separate group of compounds. Biphenyl is the first representative of the group of linear aromatic polycyclic hydrocarbons, just as the fused-ring analogue, naphthalene, is the first member of condensed aromatic hydrocarbons.

† The nomenclature based on the use of primes which has been more widely employed is adhered to in this review.

4997 (1958).
71. G. Rassel, J. Org. Chem., 24, 300 (1959).
72. C. Walling, and M. F. Mayahi, J. Amer. Chem. Soc., 81, 1485 (1959).
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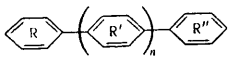
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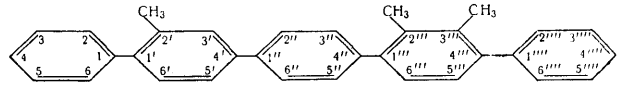
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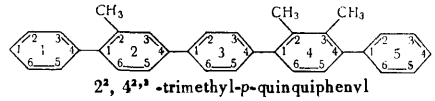
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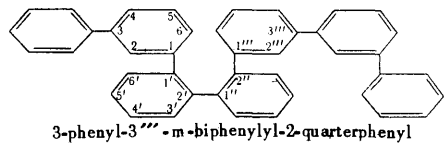
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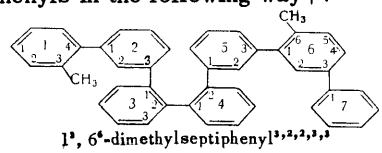
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The ever growing interest in the polyphenyls is associated with their properties and the problems connected with the chemistry and physics of these compounds (thermal stability, conductivity, optical isomerism, the mechanism of radical reactions, scintillation activity, etc.). However, the synthesis of some polyphenyls of a given structure is quite difficult; so far the interesting and in many ways unique *p*-polyphenyls containing more than 7 rings in the molecule have not been prepared. The present review is limited to the published data on the synthesis of this class of hydrocarbons as a whole; it does not extend to the preparation of branched polycyclic chain compounds. A number of surveys[2-5] have already been published on individual problems in polyphenyl synthesis.

I. SYNTHESES WITH LENGTHENING OF THE POLYPHENYL CHAIN

1. Pyrolysis

The pyrolysis of benzene has long attracted the attention of investigators, starting with Berthelot[6]. When its vapour is passed through a heated iron, porcelain, or quartz tube the main reaction product is biphenyl as well as a mixture of products of further condensation (isomeric terphenyls, triphenylene, and others[7]), carbon, hydrocarbon gases, and hydrogen. The process depends on heterogeneous catalysis. The material of the reactor[8,9] and its surface area[10] affect the yield of biphenyl. Thus at 825°, a quartz surface has a constant specific activity and the rate of reaction rises in direct proportion to the increase in surface. Migration of atoms or groups at the catalyst surface is characteristic of catalytic reactions since their migration as a result of the thermal movement of the intermediate complexes with the catalyst is energetically more advantageous than migration resulting from their own thermal movements. This accounts for the extensive recrystallisation of the glass surface within the reaction zone which has been observed[10] under these conditions, whereas in an atmosphere of nitrogen no such changes occurred even at higher temperatures. Kinetic studies[11] also suggested heterogeneous catalysis.

The range of catalysts which can be used is wide and includes pumice[12-14], alkali and alkaline-earth metal oxides and carbonates[15,16], oxides of Mo, Mg, Ba, Ca, Ce, Sr, Ti, Zr, Th, W, Mn, Cr, U, Al, V, and Be coated with graphite, zincates, vanadates, chromates, molybdates, aluminates and tungstates[17,18], K_2CO_3, ThO_2 and CoO on pumice[19], Nichrome wire[20,21], refractory clay and porcelain[9,22], activated charcoal[13], and others. The macroporosity of the catalyst[23] has been found to affect the course of reaction. Porous and non-porous catalysts behave differently presumably because of the difference in the area of catalytic surface and in the concentration of hydrogen. A rise in the latter shifts the equilibrium towards benzene[24,25]. Moreover, carbonisation occurs more intensively on porous catalysts and this lowers the yield of biphenyl calculated on the basis of the reacted benzene. The course of this side reaction is also determined by the chemical nature of the catalyst and the material of the apparatus wall[10]. In order to diminish carbonisation, it is recommended that the walls of iron and steel reactors be coated with Se, CoS, $K_2Cr_2(SO_4)_4$, $NiCl_2$, CuS, As, Si, Sb, $SbCl_3$, Sn, Sb_2S_3, Mo, MoS_x, P_2S_5, As_2S_5, SnS_x, ZnS, FeS, Zn, P[62,27], or a film of carbide[28]; addition of 0.1% of sulphur or sulphur-containing compounds to the benzene is also recommended[29].

Much research into the pyrolysis of benzene has led to industrial methods of preparation of biphenyl[9] and terphenyl[30-32]. For example, benzene vapour is passed through a heated inert liquid (Pb, NaCl, $CaCl_2$, etc.)[33,34] which sometimes contains partially oxidised organic compounds such as alcohols, ethers, esters or ketones[35]. The procedure is usually repeated twice, at 600°–650° and 750°–800°[9,36]. A method which can be easily carried out using apparatus for petroleum pyrolysis has been described[9]. Materials which serve for fettling chemical installations act as catalysts. The best yields (approximately 30% per cycle) have been obtained with refractory clay and porcelain at 750°–800°. Reaction under pressure[9,12,37-39] can be used to increase the yield of biphenyl and lower the reaction temperature; this can be brought down to 625°–695° if a pressure of 10–60 atm is used in steel tubes; the conversion of benzene per cycle reaches 20%[37,38].

Both laboratory and industrial apparatus for the preparation of biphenyl is quite simple and has been described repeatedly[9,20,36,40-43].

The thermal conversions of polyphenyl hydrocarbons have not been studied as extensively as the pyrolysis of benzene. The equilibrium constants of the reactions

$$2C_6H_6 \rightleftarrows C_6H_5C_6H_5 + H_2 ,$$

$$C_6H_5C_6H_5 + C_6H_6 \rightleftarrows C_6H_5C_6H_4C_6H_5 + H_2 ,$$

and of more profound condensations at 845°–920° have been found to be of the same order[25,24]. Pyrolysis of a mixture of biphenyl and benzene at 650°–950° gives a mixture of polyphenyls[44]. Terphenyl can be converted into biphenyl and benzene by heating in an atmosphere of hydrogen[45]. Thermal decomposition of *p*-terphenyl in a sealed tube has been studied in more detail[46]; at 279°–390° it only occurs to the extent of 3% over a period of 10 days, at 460° it amounts to 74%, and at 475° there is a further 2–3-fold increase in the rate of pyrolysis. The reaction products consist of H_2, gaseous hydrocarbons, biphenyl (10–20%), and higher polyphenyls (50–60%). The latter include *p*-quater-, and *p*-sexiphenyl, 3-phenyl-*p*-terphenyl, 3,4'--bis-(*p*-biphenylyl)biphenyl, 3-phenyl-*p*-quaterphenyl, and 4,4"-diphenyl-*m*-terphenyl. Pyrolysis of an equimolar mixture of biphenyl and terphenyl (480°, 2 days) gives 30.6% of biphenyl, 17.3% of *p*-terphenyl, 5% of *m*-quater- and *m*-quinqui-phenyl, 4% of 4-phenyl-*m*-quaterphenyl, 8% of 4-phenyl-*m*-terphenyl, 5% of 3-phenyl-*p*-quaterphenyl, and 30% of higher polymers including 4,4"--diphenyl-*m*-terphenyl. Thus polyphenyl hydrocarbons tend to condense together largely in the *meta*-position.

Reactions closely related to those considered above include the catalytic condensation of acetylene at 550°–725° yielding a mixture of products containing biphenyl[47-49], oxidation of benzene in the vapour phase giving biphenyl as a side product[50-52], and preparation of polyphenyls from benzene in an electric discharge[53-56].

The high-temperature transformations of alkylbenzenes are more complex than of benzene itself and yield a mixture of products with very small amounts of polyphenyls[57-59].

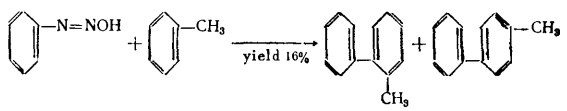
2. Preparation of Polyphenyls from Aromatic Amines

a) The Gomberg reaction. This method was proposed in 1924[60] and consists of two stages: (1) diazotisation of the aromatic amine in an aqueous medium and

(2) arylation of the aromatic hydrocarbon:

$$ArNH_2 \xrightarrow[HCl]{NaNO_2} ArN_2{}^+Cl^- \xrightarrow[NaOH]{Ar'H} ArAr'.$$

Arylation is carried out either in neutral or alkaline medium. In the former case 15–40% alkali is added gradually to a mixture of the diazonium salt solution and the hydrocarbon, in the latter the solution of the diazonium salt is added to a mixture of the aromatic hydrocarbon with a sufficient amount of dilute alkali. The reaction is usually carried out at 0°–10° but in the neutral medium it is successful even at temperatures up to 30°[61]. The choice of the method of arylation does not appear to be critical[61,62] although the second variant has been recommended[63] when the amine contains electron-donating substituents such as CH_3. The use of hydrocarbons melting above 30° raises difficulties in the choice of solvent. For example, benzenediazoniumhydroxide and biphenyl in chloroform (40°, 10 h) yielded only a small amount of *p*-terphenyl[61] since the solvent proved to be not entirely inert with respect to the diazonium compounds. This method is characterised by: (1) a low yield of polyphenyl hydrocarbons (10–25%); (2) the formation of a mixture of isomers during arylation of substituted hydrocarbons:



(the *m*-isomer was not isolated in the example cited[63] but it was almost certainly present); and (3) side reactions involving reduction of the diazo group and formation of a high-boiling tar including azo compounds and linear polyphenyls. For example, when benzene reacts with diazotised *p*-toluidine isomeric 4-methylquaterphenyls[64] are formed in addition to the main product, and when it reacts with diazotised mesitidine, 5,7-dimethylindazole and 3-mesitylenazo-5,7-dimethylindazole[65] are formed. Other alkaline agents were tried instead of NaOH in an attempt to reduce tar formation and increase the yield of polyaryl compounds. The yield of biphenyl increases by 5–10% when $Mg(OH)_2$ and $Ca(OH)_2$ are used[2] but is lowered somewhat with CH_3COONa[66]. Salts added to the reaction mixture only raise the yield in isolated cases[61,67].

Polyphenyls can be obtained without an alkaline agent[68]. Biphenyl is formed when trifluoroacetic acid, or its salt, is added to a mixture of an aqueous solution of phenyldiazonium chloride and benzene; the yield drops if the aqueous phase is diluted. The same result is achieved if the amine is diazotised in an aqueous solution of trifluoro- and trichloroacetic or perfluorobutyric acids, and is then mixed with benzene. Solid diazonium salts of perhalogeno carboxylic acids can also be used. The authors suggest that the diazotised amines exist in ionic and covalent forms in equilibrium, the latter reacting with the aromatic hydrocarbon.

b) Synthesis through *N*-nitrosoanilides. Diazonium acetates can also react with aromatic hydrocarbons, since sodium acetate can replace NaOH. Sodium diazotates can react with a mixture of acyl chloride and an aromatic compound to give biaryls[69]:

$$ArN{=}NONa \xrightarrow[NaCl]{RCOC-} ArN{=}NOCOR \xrightarrow{Ar'H} ArAr' + N_2 + RCOOH.$$

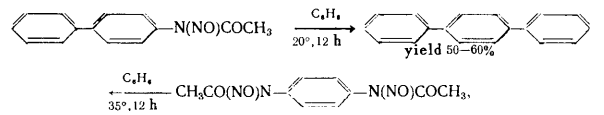
N-nitroso-*N*-arylacetamides, which are tautomers of diazonium acetates were used as arylating agents by Bamberger[70]:

$$ArN(NO)COCH_3 \rightleftarrows ArN{=}NOCOCH_3.$$

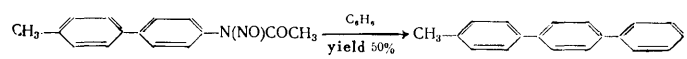
Subsequently they found preparative application.

N-Acetylarylamines are nitrosated in glacial acetic acid and acetic anhydride using nitrogen oxides ($NO + NO_2$)[71] or nitrosyl chloride in the presence of fused acetate and a small amount of P_2O_5[72]. Alkyl nitrites and sodium nitrite in trifluoroacetic acid anhydride can also be used[68]. Other *N*-acylamines can be employed instead of *N*-acetylamines[71,73]. *N*-acetyl-*N*-nitrosoarylamines dissolve in aromatic hydrocarbons and react with them completely in 12–48 h at room temperature. The reaction is more vigorous at an elevated temperature but the yield of biaryl usually falls[70,74]. Therefore temperatures of 35°–60° are only used with sufficiently stable nitroso compounds[1,71,73,75]. The yield is usually higher than in the Gomberg reaction (20–70%); it decreases to some extent when large quantities of reagents are employed since tar is formed in greater amounts[62,74].

As in the Gomberg reaction there are usually several routes towards the desired polyphenyl and the choice falls on that which avoids the formation of a mixture of isomers[76–79]. For example, *m*- and *p*-terphenyl can be prepared from *N*-nitroso-*N*-acetylaminobiphenyls and from *N*, *N*'-dinitroso-*N*, *N*'-diacetylphenylenediamines[72,73,80,81],

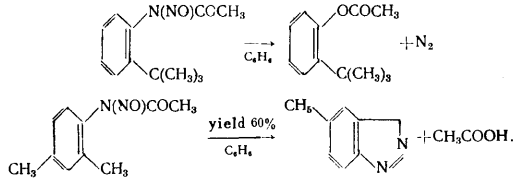


but only biphenylamines are suitable for the preparation of unsymmetrical 2- and 4-methyl-*p*-terphenyl[75]:



When the second component is a substituted aromatic hydrocarbon, a mixture of all the possible isomers is formed. Since the alkylbenzene molecule has two *o*- and *m*- and one *p*-position the "normal" ratio of the isomers should be 2 : 2 : 1. The reaction product of *N*-nitrosoacetanilide with toluene consists of 62% *o*-, 20% *m*-, and 18% *p*-methylbiphenyl[76]. The methyl group in the toluene molecule thus relatively activates the *o*- and deactivates the *m*--position for arylation (*o*-, *p*-directing group). The ratio of the *o*- and *m*-isomers alters when cumene and t-butylbenzene are used. The isopropylbiphenyl obtained contains 26% *o*-, 53% *m*-, and 21% *p*-substituted isomers, the t-butylbiphenyl contains 15, 63, and 22% (approximately) of the isomers respectively. The decrease in *o*-substitution is presumably due to steric hindrance. The *m*-directing effect of the isopropyl and t-butyl groups, with a constant amount of the *p*-isomer, may be explained by the predominance of the induction effect over the mesomeric effect.

However, not all *N*-nitroso-*N*-acetylarylamines react with aromatic hydrocarbons. Thus, *N*-nitroso-*o*-t-butylacetanilide in benzene yields principally *o*-t-butylphenyl acetate[76] and *N*-nitroso-2,4-dimethylacetanilide gives 5-methylindazole[77].



c) Direct synthesis from diazonium salts. Dry diazonium salts react with excess aromatic hydrocar-

bon on heating [82]. Benzenediazonium chloride decomposes in a mixture of benzene, acetone, and chalk (for neutralisation) to give up to 25% of biphenyl [83]:

$$2C_6H_5N_2Cl + 2C_6H_6 + CaCO_3 \rightarrow 2C_6H_5C_6H_5 + 2N_2 + CaCl_2 + H_2O + CO_2.$$

The reaction can be carried out at room temperature by adding zinc dust to the reaction mixture and the double salt of diazonium chloride with $ZnCl_2$ can be used. $AlCl_3$ serves as a good catalyst at higher temperatures [82,84].

Stabilised diazonium salts in ether react also with arylmagnesium halides [85,86]:

$$ArN_2Cl \cdot 0.5ZnCl_2 + Ar'MgBr \rightarrow ArAr' + MgClBr + 0.5ZnCl_2 + N_2.$$

In some cases biaryls can be derived from the aryl groups of the initial salt only. The Gatterman reaction which involves the decomposition of diazonium salts in the presence of powdered copper,

$$ArN_2X \xrightarrow[Cu]{} ArX + N_2$$

gives biaryls in an alcoholic medium [87]. The greater the amount of alcohol, the greater the formation of linear polyphenyls with a large number of rings in the chain. Under these conditions benzenediazonium sulphate yields 16.8% of biphenyl, ~ 7.8% of *p*-terphenyl, 5.5% of quaterphenyl, and 0.8% of *p*-quinquiphenyl [88]. When alcohol is replaced by anhydrous formic acid (diazotisation in acetic acid) the yield of biphenyl is 10.3% and of *p*-polyphenyls 24.8% [89]. Biphenyl has been prepared in 50% yield by the action of copper powder on benzenediazonium sulphate in acetic anhydride [90]. A small amount of biphenyl (up to 5%) has been isolated on decomposition of a suspension of benzenediazonium chloride in acetone in the presence of various elements, including Ag, Au, Cd, Sn, Pb, Ni, Bi, B, and others [83], and on reduction of stabilised diazonium salts with organomagnesium compounds, for example $C_6H_5N_2Cl \cdot 0.5\,ZnCl_2$ with ethylmagnesium bromide [91].

d) Other methods. A small amount of biphenyl is formed when phenylazotriphenylmethane undergoes thermal decomposition in benzene [92]. Since the solvent takes part in the reaction, toluene yields a mixture of isomeric methylbiphenyls [93]. This is a theoretically interesting reaction but unsuitable for preparative use since only one of the phenyl groups of the initial compound (22 wt. %) enters the biaryl molecule if the formation of $(C_6H_5)_4C$ is disregarded:

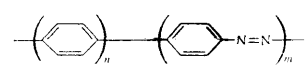
$$C_6H_5N{=}NC(C_6H_5)_3 \xrightarrow{ArH} C_6H_5Ar + (C_6H_5)_3CH + N_2 [+ \text{small quantity of } (C_6H_5)_4C].$$

This objection applies equally to the use of triazens ($RN{=}N{-}NR'R''$). When a 4% solution of diazoaminobenzene in cumene is heated for 40 h at 160° the products include, among other substances, isopropylbiphenyls [94]:

$$C_6H_5N{=}NNHC_6H_5 \xrightarrow{C_6H_4CH(CH_3)_2} C_6H_5C_6H_4CH(CH_3)_2 + (C_6H_5)_2NH +$$
$$+ C_6H_5NH_2 + (CH_3)_2\underset{C_6H_5}{\overset{}{C}}{-}\underset{C_6H_5}{\overset{}{C}}(CH_3)_2 + N_2.$$

Isomeric substituted biphenyls are formed from 1-phenyl-3,3-dimethyltriazen in alkyl benzenes with yields of 18–22% [76] and in practically the same ratios as in the phenylation of *N*-nitrosoacetanilide. 1-*o*-Tolyl-3,3-dimethyltriazen in boiling benzene and acetic acid yields 9% of 2-methylbiphenyl and 21% of indazole [95].

Polyphenyl hydrocarbons are not infrequently formed by the deamination of arylamines. Sodium benzenediazoate is reduced by alcohol giving 50% of benzene and 25% of biphenyl [96]. When deamination is effected with hypophosphorous acid, biphenyl (9.1%) and *p*-terphenyl (2.6%) are formed as by-products [97]. It is interesting that when the bisdiazonium compound from benzidine is treated with activated copper or an ammoniacal solution of cuprous oxide to obtain a macromolecular product, only the nitrogen-containing polymer of the following structure [98–100] can be obtained:



3. Arylation with Aromatic Acid Peroxides. Mechanism of Arylation

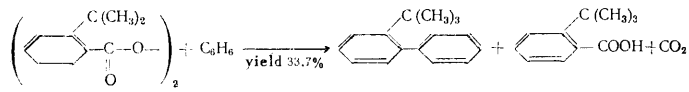
The main products of the reaction between benzoyl peroxide and boiling benzene are biphenyl and benzoic acid [101]. Peroxides of monosubstituted acids yield only monosubstituted biphenyls. The main reaction can thus be represented by the equation

$$(ArCOO)_2 + Ar'H \rightarrow ArAr' + ArCOOH + CO_2.$$

In practice, however, the reaction is much more complex. Gelissen and Hermans [101] isolated not only biphenyl (yield 26%) and benzoic acid, but also an appreciable amount of *p*-quaterphenyl, phenyl benzoate, and *p*-terphenyl. If the reaction is carried out at 78° and an initial concentration of the peroxide equal to 2–10%, the composition of the reaction products corresponds to the following stoichiometric equation [102]:

$$1.00\,(C_6H_5COO)_2 + 0.98C_6H_6 \rightarrow 1.19CO_2 + 0.42C_6H_5COOH + 0.04C_6H_5C_6H_4COOH +$$
$$+ 0.40C_6H_5C_6H_5 + 0.06C_6H_5COOC_6H_5 + 0.01C_6H_5C_6H_4C_6H_5 + 0.025C_6H_5C_6H_4C_6H_4C_6H_5 +$$
$$+ 0.05\,(C_6H_5COO)_2O + 0.05H_2O + 0.06C_6H_5C_6H_5C_6H_5C_6H_5 \text{ (“quinhydrone type” structure)} + \text{high-boiling residue (composition } 0.50\ C_6H_5,$$
$$0.40\ C_6H_4,\ 0.15\ C_6H_5COO).$$

The choice of reagents for the synthesis is governed by the same considerations as those discussed for the other methods of arylation. For example, individual t-butylpolyphenyls can be prepared using substituted peroxides but not t-butylbenzene [79].



A mixture of isomers is always formed when substituted hydrocarbons are used, e.g. fused biphenyl treated with benzoyl peroxide for 13 h at 78° gives 64% of isomeric terphenyls [103]. In reactions of this type the quantitative proportions of the isomers are independent of the reagents used (peroxide, *N*-nitrosoacetanilide, etc.) and reflect the directing effect of the substituent [76]. Comparison of the rate of phenylation of the substituted hydrocarbon with that of benzene indicates the effect of the substituent on the reactivity. The benzoyl peroxide reaction is particularly convenient for this [102]. The relative rates are measured by the "competitive substitution" method [104]. The peroxide is decomposed in an excess of an equimolar mixture of

benzene and the hydrocarbon in question (usually at 80°); the excess must be sufficient to prevent a substantial change in the molar composition of the mixture as a result of the different rate of disappearance of the components. This gives

$$K_H^R = \frac{\text{rate constant for } C_6H_5R \text{ phenylation}}{\text{rate constant for } C_6H_6 \text{ phenylation}} = \frac{\text{amount of } C_6H_5C_6H_4R}{\text{amount of } C_6H_5C_6H_5}.$$

The two separate characteristics of the substituent effect (isomer ratio and K_H^R) can be combined into one, expressed by the partial-rate factors. These are the factors (F) which relate the rate of substitution at a given carbon atom to that at a benzene carbon atom. The rate of substitution in an alkylbenzene equals the sum of the rates of substitution at the two *ortho*-, two *meta*-, and one *para*--positions:

$$V = 2V_o + 2V_m + V_p.$$

The rate of reaction at each benzene carbon atom is taken to be unity and the total rate therefore equals 6. Hence for C_6H_5R

$$6K_H^R = 2F_o + 2F_m + F_p$$

and

$$F_p = \frac{6K_H^R c}{100}, \quad F_m = \frac{3K_H^R b}{100}, \quad F_o = \frac{3K_H^R a}{100},$$

where a, b, and c represent the percentage content of the isomer in the mixture. If R = C_6H_5 the number of these positions in the hydrocarbon doubles and therefore

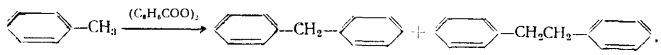
$$F_p = \frac{3K_H^{C_6H_5}c}{100}, \quad F_m = {}^3/_2\,\frac{K_H^{C_6H_5}b}{100} \text{ and } F_o = {}^3/_2\,\frac{K_H^{C_6H_5}a}{100}.$$

Data from various sources are summarised in the Table.

The effect of the substituent on the rate of hydrocarbon phenylation.

R	K_H^R	Amounts of isomers, %			F_o	F_m	F_p	References
		o	*m*	*p*				
CH_3	1.9	62—70.8	16.7—25	12.4—17	3.5—4.0	1.0—1.2	1.4—1.9	76,77,105, 106
C_2H_5	1.2	50	25	25	1.8	0.9	1.8	77,106
$(CH_3)_2CH$	0.87	10—29	50—60	21—30	0.3—0,8	1.3—1.6	1.1—1.6	106,76,77
$(CH_3)_3C$	0.87	17—24	49—62	22—27	0.5—0,6	1.3—1.6	1.1—1.4	76,77,79
C_6H_5	4.0	48.5	23	28.5	2.9	1.4	3.4	107
1,2-CH_3,CH_3		63		37				77
1,4-$(CH_3)_2$C, $(CH_3)_3$C	0.63		100				0.95	79

These results indicate that arylation reactions using both peroxides and nitrogen-containing compounds are homolytic[62,77,108] (for a detailed account see ref. 109). Substituents like the nitro group in this case activate the ring and direct the incoming aryl group to the *o*- and *p*--positions, unlike the situation in electrophilic-substitution reactions. The differences in the reactivity of the *o*-, *m*- and *p*-positions are relatively small (Table), whereas in heterolytic substitutions these differences are considerably greater, since the position of entry is controlled by the charge of the species and polarity of the substituted aromatic ring. Further evidence for a homolytic mechanism comes from the appearance of such side products as polyphenyls and compounds formed by the action of the attacking agent on the side chains of the hydrocarbon undergoing arylation[76,77,106]:



In general, homolytic reactions can occur in several ways[110]: (1) the radicals generated enter the bulk of the reaction mixture and give an intermediate complex with the substrate; chain reactions are also possible with splitting off of the peripheral atom by the radical (radical transfer) $-R\cdot + X:Z \rightarrow R{\cdot}X:Z$; $R\cdot + X:Z \rightarrow R:Z + X\cdot$; (2) the initial reagents form an intermediate complex $R:S + X:Z \rightarrow R:SX:Z$; (3) the compound K:S, being solvated, decomposes into radicals which recombine without entering the bulk of the solvent, a process similar to that occurring on the surface of finely-divided metals[111].

A free-radical mechanism has been postulated for arylation[62,92], suggested by the following evidence: (a) the ability of arylating agents to undergo spontaneous decomposition in the absence of the second component; (b) the constant rate of monomolecular breakdown of benzenediazonium acetate in various solvents (in fact the velocity constants are not identical but are of the same order of magnitude[62,74]: in benzene $K_{20°} = 0.00461$, in *m*-xylene 0.00466, in toluene 0.00344, in mesitylene 0.00507, in carbon tetrachloride 0.00405, and so on); (c) the independence of the ratio of the isomeric polyphenyls obtained of the phenylating agent and consequently of the reaction temperature which is governed by the choice of the agent. Nonetheless, this mechanism is not the only possible one[112]. Work with labelled atoms[110,111] has shown that whereas free phenyl radicals do arise in the decomposition of benzoyl peroxide, a cryptoradical mechanism must underlie arylation with *N*-nitrosoacetanilide. On testing for free radicals by their exchange with benzene, it was found that in the case of benzoyl peroxide some of the "primary" radicals are converted into benzene:

$$\dot{C}_6H_5 \cdot \xrightarrow{C_6H_6} \dot{C}_6H_6 + C_6H_5\cdot,$$

and the radicals formed from the solvent can be trapped by mercury acetate:

$$C_6H_5\cdot \xrightarrow{\dot{C}_6H_6} C_6H_6 + \dot{C}_6H_5, \qquad \dot{C}_6H_5\cdot \xrightarrow{(CH_3COO)_2Hg} \dot{C}_6H_5HgOCOCH_3.$$

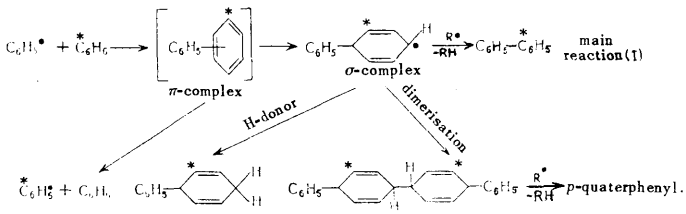
No transfer of radicals was discovered in the case of *N*--nitrosoacetanilide:

$$\dot{C}_6H_5N{=}NOCOCH_3 + C_6H_6 \rightarrow \dot{C}_6H_5C_6H_5 + N_2 + CH_3COOH$$

$$C_6H_5N{=}NOCOCH_3 \xrightarrow[\dot{C}_6H_6]{Hg} C_6H_5HgOCOCH_3 + N_2.$$

Thus arylation with benzoyl peroxide consists of the following sequence of events: breakdown into radicals, combination of a radical with the hydrocarbon molecule, and splitting off of a hydrogen atom by another radical[113,114]. During the attachment of the radical a π-complex, which is probably formed first, is either converted into a σ-complex or undergoes another internal rearrangement[110]. Isolation of 1,4-dihydrobiphenyl and 1',4',1'',4''-tetrahydro-*p*--quaterphenyl[115] from the reaction products and the carbon isotope evidence suggests the following scheme for the

course of the reaction[116]:



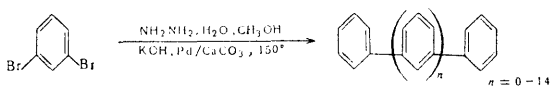
p-Terphenyl is probably formed from biphenyl in a way similar to reaction (I)[116,117].

4. Preparation of Polyphenyls from Aryl Halides

(*a*) Reduction using a palladium catalyst. Aryl halides can be reduced by a 4–6% solution of alkali in methanol using a $Pd/CaCO_3$ catalyst at temperatures up to 135°–150°[118,119]. Bromobenzene treated in this way gives 35% of biphenyl[120]. The yield rises to 50.4% when methanol is diluted with water and to 75% when hydrazine hydrate is added[118,119].

The formation of biaryls depends primarily on the specific properties of the catalyst, the choice of the reducing agent and the presence of an adequate amount of strong alkali. When the catalyst is poisoned by small amounts of nickel or copper salts, which do not affect the parallel reduction of bromobenzene to benzene, the yield of biphenyl drops to 5% or less. No biphenyl is formed when nickel, platinum and copper catalysts, or even palladium on a polyvinyl alcohol carrier, are used. Methanol cannot be replaced as a reducing agent by ethanol or isopropyl alcohol, presumably because of differences in the ease of their dehydrogenation and the action of the condensation products of the resulting aldehyde or ketone on the catalyst. In the presence of hydrazine, to which is ascribed the role of an aldehyde-binding agent, ethanol and dioxane as well as methanol can be employed[119].

This method has been used for the synthesis of higher polyphenyls[119]. *p*-Dibromobenzene treated in an autoclave at 150° yields 21% of biphenyl, 14% of *p*-terphenyl, 10% of *p*-quaterphenyl, 2% of *p*-quinquiphenyl, 0.7% of *p*-sexiphenyl, and 0.2% of *p*-septiphenyl. *m*-Dibromobenzene gives an 86% yield of *m*-linked hydrocarbons containing up to 16 aromatic rings in the molecule:



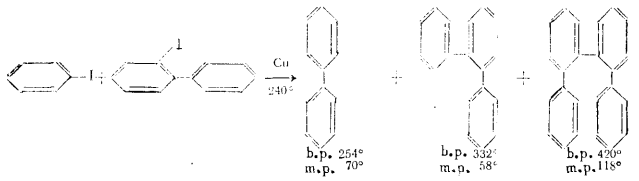
The mechanism of the reaction has not been adequately investigated. Formation and recombination of radicals on the catalyst surface has been postulated[120].

(*b*) The Ullmann reaction. This consists of removing the halogen from two molecules of aryl halide using copper, and is one of the most useful methods for the preparation of polyphenyl hydrocarbons[1,81,118,121–144]:

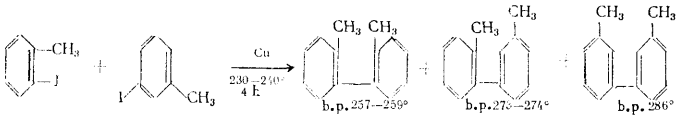
$$ArX + Ar'X' + Cu \rightarrow ArAr' + CuXX'.$$

The reaction is carried out at 200°–330°, depending on the reactivity of ArX (X is usually I), in a sealed tube[121] or autoclave[137] if necessary. The use of a solvent prevents local overheating and in some cases enhances the yield of the biaryl. For example, the yield of 3,3'-dimethylbiphenyl from *m*-iodotoluene is 55% in boiling dimethylformamide (72 h)[122], whereas without solvent (205°–240°, 3 h) it is only 35%[121]. If the initial compounds have substituents in the 2,6-positions, the yield of biaryl drops owing to steric hindrance; the yield of dixylyl from 2,6-dimethyliodobenzene at 240°–265° is only 21%[125] and that of bimesityl does not exceed 12.5%[121,126].

The preparation of unsymmetrical polyphenyl hydrocarbons by this method is further complicated by the formation of a mixture of three products. This problem is rendered easier if the reaction gives a mixture of polyphenyls with a different number of rings[130]:



Otherwise the separation of the hydrocarbons is extremely difficult. For example, 3 bitolyls were obtained from a mixture of *o*- and *m*-iodotoluene[137]:



Only the 2,2'-isomer could be separated satisfactorily by distillation. Two other fractions contained a mixture of 2,3'- and 3,3'-bitolyl which were only separated after oxidation to biphenyldicarboxylic acids. The use of disubstituted aryl halides opens up interesting possibilities. The reaction between 4,4-diiodobiphenyl and 4-iodobiphenyl yields 24.4% of *p*-sexiphenyl[143]; 3,3'-dimethyl-4,4'-diiodobiphenyl in α-methylnaphthalene gives higher polyaryls with molecular weights of 1000–300 000 but probably with a branched structure[141,142].

Attempts to replace copper by other metals (Mg, Zn, Fe, Ag) proved unsuccessful[121], although silver is effective in the synthesis of certain polycyclic hydrocarbons[89,123,143], e.g. *p*-sexiphenyl from 4-iodo-*p*-terphenyl at 330°[123]. With copper the reaction is sluggish at 300° and only specially activated copper yields a small amount of the desired product[143].

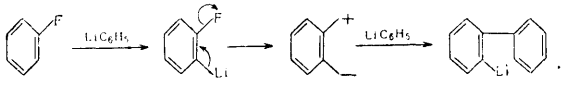
The mechanism of the Ullmann reaction has not yet been fully clarified. A free-radical mechanism has been postulated on the basis that, when ethyl benzoate is added to the reaction mixture of iodobenzene with copper, the products include esters of 2- and 4-biphenylcarboxylic acids[145]. The absence of characteristic polymeric side products and a number of other facts[3] suggest recombination of radicals on the surface of the finely divided metal or an activated-complex stage in the reaction, without generation of kinetically independent species. The possibility of intermediate organocopper compounds is also not excluded.

(*c*) The Wurtz-Fittig reaction. Although aryl halide condensation with the help of alkali metals has been known for nearly 100 years[146,147], this method has been applied to relatively few polyphenyl hydrocarbons. Probably, the use of aryl dihalides yields the most interesting results[148–152]. Polycondensation of dichlorobenzene using sodium or a liquid sodium-potassium alloy (KNa_2) gives a

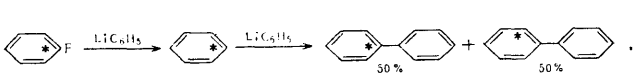
polymeric product, so-called "polyphenyl" [151,152]. The alloy is introduced gradually into a boiling solution of *p*-dichlorobenzene in dioxane; after prolonged heating the polymer is isolated with an 80% yield, of which approximately 90% is soluble in benzene. The molecular weight of this soluble polyphenyl is of the order of 2700–2800 (±500); it contains 4.9 ± 0.9 chlorine atoms per mole, so that the molecule consists on average of 34 benzene rings some of which appear to have a quinonoid structure. The rings are presumed to be joined together in the *p*-position [151] and the molecular chain is probably branched [141]. "Polyphenyl" is highly thermostable but friable. Its friability and the rigidity of the polymer chain preclude its practical use [153,154].

A methylated polymer has also been obtained [141,142], by condensation of 3,3'-dimethyl-4,4'-diiodobiphenyl with sodium in toluene; the reaction product is partially soluble in benzene and has a branched-chain molecule.

The Wurtz-Fittig-synthesis consists of two stages: (1) formation of an arylsodium and (2) its reaction with more arylhalide [155]. The second stage is accompanied by the formation of a number of side products [156–158] such as *o*- and *p*-terphenyl, triphenylene, and hydrocarbon tar [130,157,159]. The arylsodium is presumably formed by ArBr reacting successively with two neighbouring sodium atoms with the appearance of radicals on the metal surface [156,160]. This type of reaction was investigated with phenylithium [156,161] and it was unexpectedly found that the most reactive compound was fluorobenzene despite the well-known inertness of the fluorine atom in it. Under identical conditions it yielded 8 times as much biphenyl as did iodobenzene. The intermediate product – 2-lithiumbiphenyl – was isolated with the help of benzophenone. The inductive effect of the strongly electronegative fluorine apparently enhances the mobility of the hydrogen atom in the *o*-position of the initial aryl halide which is replaced by lithium. This substitution by the considerably more electropositive lithium leads to splitting off of the fluoride anion and formation of benzyne which then condenses with the second molecule of phenyllithium:



The nature of the bonds formed in the benzyne ring has not been established precisely. Work with labelled atoms [162] has shown that 50% of the phenyllithium molecules enter the position formerly occupied by fluorine and 50% the positions *ortho* to it. This suggests the formation of a new π-electron cloud in the plane of the benzene ring.



Data on benzyne have been considered in detail [163].

(*d*) The Grignard synthesis. As already mentioned, Ullmann's attempt to use magnesium for the preparation of biphenyl failed. The Grignard reagent prepared beforehand might have been supposed to react with aryl halide, but boiling phenylmagnesium bromide with iodo- or bromobenzene in ether, toluene, or without solvent (140°–180°) only gave a very low yield of biphenyl (10–13%) [164,165]; the yield could be raised a little by carrying out the reaction at 150°–200° in an autoclave [166]. Preparative methods of obtaining polyphenyls from organomagnesium compounds only became possible with the use of certain metal halides. One of these consists in oxidation of ArMgX, usually in boiling ether, with stoichiometric amounts of salts such as $CuCl_2$ [124,126,134,167–170], AgBr [171,172], $MoCl_5$ [173], $CoCl_2$ [167], $CrCl_3$ [168,169], and others [174]:

$$2ArMgBr + 2CuCl_2 \rightarrow ArAr + Cu_2Cl_2 + 2MgBrCl\,.$$

Preliminary preparation of the Grignard reagent is not always necessary and sometimes even undesirable; for example, biphenyl-4-ylmagnesium bromide gives a 52% yield of *p*-quaterphenyl whereas boiling a mixture of 4-bromobiphenyl with magnesium and $CuCl_2$ in ether gives a 63% yield [124]. The oxidation reaction occurs in two stages [175,176]:

$$ArMgX + MX \rightarrow ArM + MgX_2,$$
$$2ArM \xrightarrow{(O_2)} ArAr + 2M \quad (M_2O).$$

The reaction between phenylmagnesium iodide and CuI at 0° in an atmosphere of nitrogen yields phenylcopper [175] which, on decomposition (20°), atmospheric oxidation, and other transformations, gives biphenyl. Phenylsilver prepared from phenylmagnesium bromide and AgBr at -18° behaves similarly [175,176]. An interesting phenomenon was demonstrated by using copper sulphate as the oxidising agent [168]. Owing to its extremely low solubility in ether, it reacts with phenylmagnesium iodide with great difficulty; however, when iodobenzene is added to the reaction mixture, biphenyl is formed smoothly according to the equation

$$4C_6H_5MgI + 2C_6H_5I + 2CuSO_4 \rightarrow$$
$$\rightarrow 3C_6H_5C_6H_5 + 2MgSO_4 + 2MgI_2 + Cu_2I_2.$$

Thus half of the initial phenylmagnesium iodide is oxidised not by the metal salt but by iodobenzene. Preparation of polyphenyls by oxidation of ArMgX with halogen-containing compounds in the presence of small amounts of metal salts was discovered independently of the above observation, during a search for catalysts of the reaction

$$ArMgX + ArX \rightarrow ArAr + MgX_2.$$

It was found [165] that an excess of bromobenzene boiled in ether for 11 h with magnesium and $FeCl_3$ (4 mole %) gave a quantitative yield of biphenyl. The yield was 65% when $CuCl_2$ catalyst was used. The reaction was later investigated in detail [177] and a mechanism was postulated for it [178]. In the presence of 2.5–7 mole % $CoCl_2$ and 0.74–0.88 mole of bromobenzene 83–86% of phenylmagnesium bromide is converted to biphenyl. The molecule of the latter does not contain phenyl groups from the free bromobenzene which can be successfully replaced by alkyl and other aryl halides [177,179,180]. In accordance with this *p*-tolylmagnesium bromide and bromobenzene with $CoCl_2$ yield 95% 4,4'-dimethylbiphenyl [177].

The following scheme is proposed for this process:

$$ArMgX + CoCl_2 \rightleftharpoons ArCoCl + MgClX,$$
$$2ArCoCl \rightleftharpoons ArAr + 2CoCl.$$

The halogenated derivative reacts with cobalt subhalide regenerating the salt of the divalent metal and forming a radical:

$$CoCl\cdot + RX \rightarrow CoClX + R\cdot\,.$$

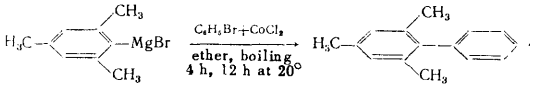
The side products arise through further transformations of this radical. Thus when C_4H_9MgBr reacts with C_6H_5Br and $CoCl_2$ the products include 44% of C_6H_6, 3% of $C_6H_5C_6H_5$, and 11% of other polyphenyls [179].

$$xC_6H_5 \rightarrow C_6H_6 + C_6H_5C_6H_5 + C_6H_5C_6H_4C_6H_5 + (C_6H_5C_6H_4)_2 + \ldots$$

If the oxidising agent is an alkyl halide, however, no

high-boiling polyphenyls are formed. In the absence of RX the cobalt subhalide can be disproportionate and be oxidised by atmospheric oxygen.

In spite of Kharasch's scheme an unsymmetrical product can be formed in this reaction as well, presumably because of the radical mechanism of arylcobalt chloride decomposition. For example, phenylmesitylene has been prepared (yield 18.4%) from mesitylmagensium bromide and a four--fold excess of bromobenzene[167]:

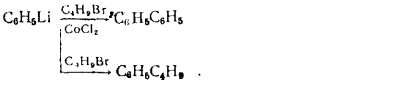


Nickel chloride, ferrous chloride, and other substances can also be used as catalysts[177,181]. The Grignard reaction proved to be of little value for the preparation of methylated polyphenyl from 4,4'-diiodo-3,3'-dimethylbiphenyl and 2,5--dibromotoluene[182]. Khorschak[183,184] discovered and studied the preparation of polyphenyls from arylmagnesium halides and hexachloroethane without addition of salts:

$$2ArMgX + C_2Cl_6 \rightarrow ArAr + MgXCl + C_2Cl_4.$$

This method gave a 35% yield of biphenyl from phenylmagnesium bromide at 22°. Thanks to the intermediate formation of radicals, a solution of the Grignard reagent initiates styrene polymerisation more energetically in the presence of hexachloroethane.

(*e*) Preparation of polyphenyls from other organometallic compounds. Certain other organometallic compounds behave similarly to the Grignard reagents; for example, phenyllithium is oxidised by butyl bromide in the presence of $CoCl_2$ giving a 67% yield of biphenyl, whereas in the absence of the salt the usual Wurtz-Fittig synthesis takes place[180]:



2,2'-Dilithiobiphenyl in the presence of $TiCl_4$, $CuCl_2$, $MnCl_2$, $FeCl_2$, or $CoCl_2$ forms a mixture of aromatic hydrocarbons including biphenyl (up to 79%), *o*-quaterphenyl (up to 38%), *o*-sexiphenyl (up to 8%), and *o*-octaphenyl (up to 1.4%)[185].

When phenylaluminium diiodide is heated with bromobenzene in benzene it is converted to biphenyl (97.7%)[186].

$$2C_6H_5AlI_2 \xrightarrow[1\ h]{245°-255°} C_6H_5C_6H_5 + 2AlI_2,$$

$$AlI_2 + C_6H_5Br \rightarrow C_6H_5\cdot + AlI_2Br.$$

As in Kharashch's experiments, *p*-terphenyl, *p*-quaterphenyl, and *p*-quinquiphenyl are isolated. When bromobenzene is replaced by *p*-chloro- or *p*-bromotoluene, no methylbiphenyls are formed, biphenyl remaining the main reaction product (yield up to 30%).

Oxygen can also be used for the oxidation of organometallic compounds of polyphenyls. Phenyl and *p*-biphenyllithium in ether are oxidised to biphenyl (yield 65%) and *p*-quaterphenyl (yield 85%) respectively[187]:

$$4ArLi + O_2 \rightarrow 2ArAr + 2Li_2O.$$

When phenyllithium and triphenylindium are oxidised with oxygen in benzene they give phenyl (17–26%) and 20–25% of biphenyl[188,189]

Thermal decomposition of triphenylthallium[190,191] and tetraphenylchromium iodide[192] and catalytic decomposition of diphenylmercury and tetraphenyllead, in the presence of Pd and other metals[193,194] leads to the formation of biphenyl. Biaryls are also produced by photochemical reactions[195-198] and some complex reactions such as those of arylsodium or lithium with N_2O[199], arylmagnesium halides with nitroaromatic[200] and azoxy compounds[201] or with iodoaryl dichlorides[202]. They are formed also as side products, sometimes in considerable amounts, in the course of many organometallic syntheses[203-208].

5. Preparation by Elimination of Sulphur and Selenium

Biaryls are obtained by removal of sulphur from thioethers, disulphides, and thiophenols and their esters by Raney nickel or the Sabatier nickel catalyst at sufficiently high temperatures[209]:

$$Ar_2S \xrightarrow{Ni} ArAr$$

Heating is continued for 15 h in a sealed tube, either in the presence of benzene or without it. An appreciable amount of biphenyl already forms at 180°. Diphenyl disulphide, which at 140° is converted to the extent of 84–87% into diphenyl sulphide, at 180° gives 54% and at 220° 65–85% of biphenyl. If the initial compound contains two different aryl radicals, or if a mixture of two substances is taken, three hydrocarbons are formed simultaneously:

$$ArSAr' \xrightarrow{Ni} ArAr + ArAr' + Ar'Ar'$$

In some cases *p*-terphenyl (up to 6% of the theoretical amount) can be isolated from the tarry reaction products.

The nickel catalyst is first degassed at 200°. The small amount of H_2 which remains takes part in the side reaction

$$Ar_2S \xrightarrow[Ni]{H_2} ArH,$$

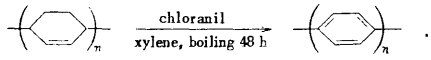
without affecting the course of the main process: the yield of biaryls is not diminished when the catalyst is degassed at 500° and is practically H_2-free. Reduced iron catalysts used for purification of industrial gases react with diphenyl sulphide at 350° also giving chiefly biphenyl[210].

Organic selenium-containing compounds behave similarly to the sulphur-containing ones. Whereas at 140° (14.5 h) diphenyl diselenide gives, with degassed Raney nickel, 21.5% of diphenyl selenide and 31% of biphenyl, at 180° 72% of biphenyl is formed in 8 h[211]. Di(*o*-methylphenyl)selenide is converted into 2,2'-dimethyl biphenyl in 52% yield.

II. SYNTHESIS WITHOUT ALTERATION OF THE CYCLIC CARBON SKELETON (DEHYDROGENATION)

Dehydrogenation of polycyclic hydroaromatic compounds is used for two purposes: (1) for the synthesis of polyphenyl hydrocarbons of a given structure and (2) for the determination of the structure of unknown hydroaromatic compounds. Dehydrogenation is effected either by the use of hydrogen acceptors or catalytically. The reaction conditions depend on the choice of dehydrogenating agent and the structure of the initial compound. The most widely used acceptors are tetrachlorobenzoquinone, sulphur, and selenium. Tetrachlorobenzonequinone (chloranil) is often preferred since it is effective at a relatively low temperature. Benzonquinone itself is a much less active dehydrogenating agent[212].

When an excess of chloranil is used in boiling xylene (140°–145°), dehydrogenation to aromatic compounds occurs within 4–48 h. Saturated cyclic hydrocarbons are not dehydrogenated under these conditions [213]. The reaction evidently follows a radical mechanism [213]. This method has been used for the synthesis of a number of two to six-ring polyphenyls from hydrocarbons containing, in the polycyclic chain, cyclohexane, cyclohexadiene, and aromatic units [1,167,212,214–218]. It is noteworthy that the best conversion of poly-1,3-cyclohexadiene to polyphenyl also occurs when chloranil is used [219]



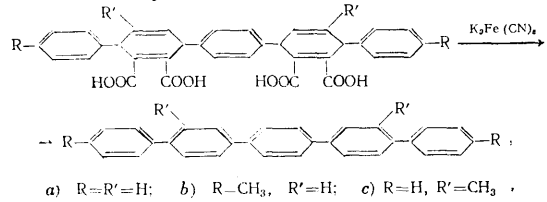
Dehydrogenation with sulphur usually occurs within 1.5–5 h at 180°–250°. Longer heating is sometimes necessary [80,220]. A solvent is used in some cases (quinoline) [80,221]. Substituted arylcyclohexenes [80,134,220,222–226], and less frequently cyclic alcohols and hydrocarbons, of varying degrees of unsaturation [223,227–229] undergo aromatisation. An interesting observation made during the synthesis of dimethylbiphenyls [133] is that a mixture of sulphur and palladised charcoal is more effective than either component individually: the reaction is more rapid and takes place at a lower temperature (190°–200°). Dehydrogenation with sulphur is sometimes complicated by the migration of a mobile alkyl group: attempts to obtain 3- and 4-t-butylbiphenyl failed though migration of the t-butyl group and formation of a mixture of isomers [76].

Selenium is often used for the preparation of polyphenyls especially from aryl substituted cyclohexanes [230–238]. Dehydrogenation occurs at 320°–370°. Other dehydrogenating agents are only used in isolated cases, e.g. bromine at 160° [237,238], diphenyl disulphide at 250°–260° [239], and *N*-bromosuccinimide in carbon tetrachloride [240].

The most frequently used catalyst is probably palladium on activated charcoal. It has been used for the synthesis of polyphenyl hydrocarbons containing up to 8 aromatic rings [77,133,241–249]; Pd/Al_2O_3 [250,251], Pt/C [230,252], Pt/Al_2O_3 [253], Cr_2O_3/Al_2O_3 [254–257], and reduced nickel chromite [258] are also suitable.

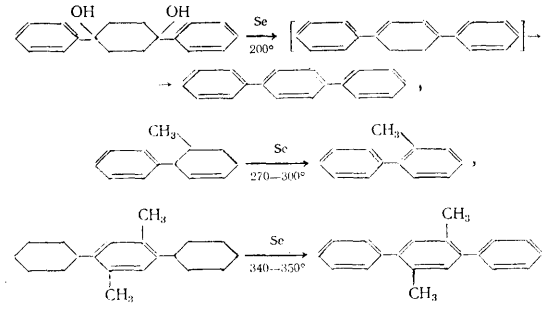
Some general comments can be made on the variation of the conditions necessary for the dehydrogenation of polycyclic hydroaromatic compounds with their structure.

1. As expected, the greater the number of double bonds in the initial molecule, the easier its transformation into an aromatic system. Therefore aryl-substituted cyclohexadienes show the greatest tendency to dehydrogenation. 1,3-Dipehnylcyclohexa-1,3-diene undergoes autooxidation on standing [242], its *p*-isomer loses hydrogen on distillation [225], and phenylcyclohexadiene hydrogenated with palladised charcoal at 20° forms, through irreversible catalysis, a mixture of biphenyl and phenylcyclohexane [259]. If the diene ring contains carboxyl groups, as in the case of 3,6-diphenyl-3,6-dihydrophthalic acid [260] or of tetracarboxylic acids of tetrahydro-*p*-quinquiphenyls [261], simultaneous oxidation and decarboxylation occur on gentle heating with potassium ferricyanide solution:

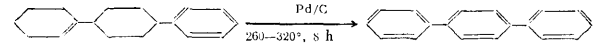


a) R=R'=H; *b*) R–CH_3, R'=H; *c*) R=H, R'=CH_3.

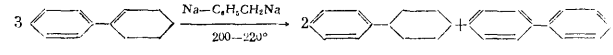
The increasing difficulty of dehydrogenation with increasing saturation can be traced in several examples. Whereas 1,4-diphenylcyclohexane-1,4-diol gives *p*-terphenyl with selenium at 200° [262], 2-phenyl-Δ^3-tetrahydrotoluene is not converted to 2-methylbiphenyl below 270°–300° [263], and 1,4-dimethyl-2,5-dicyclohexylbenzene only undergoes aromatisation at 340°–350° [264]:



Diarylcyclohexadienes are converted smoothly into polyphenyls when palladium in boiling cymene (177°) is used [242,244–247]; however, when *p*-terphenyl is prepared from 1-phenyl-4-(cyclohexen-1'-yl)cyclohexane heating has to be continued for 8 h at 260°–320° [248]:

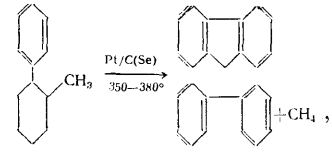


The role of a double bond conjugated with the phenyl ring is clearly seen on comparison of the dehydrogenation of 1-phenylcyclohexene and phenylcyclohexane. The former is converted to biphenyl to the extent of 52% in 4 h using chloranil [212], whereas the latter gives only 13% of the product after 16 h heating with a larger amount of the reagent [213]. In the presence of sodium–benzylsodium catalyst, 1-phenylcyclohezene disproportionates almost quantitatively at 200°–220° [265]:



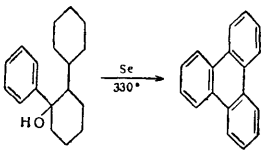
but the phenylcyclohexane so obtained requires a higher temperature (above 240°) for dehydrogenation.

2. The presence of a substituent in the position *ortho* to the internuclear bond may lead to undesirable side reactions and requires particular care in the choice of experimental conditions. Thus 1-methyl-2-phenylcyclohexane treated with 20% platinised charcoal at 350°–380° or dehydrogenated with selenium gives fluorene as the main product; simultaneously elimination of the methyl group leads to the formation of some biphenyl [251]:

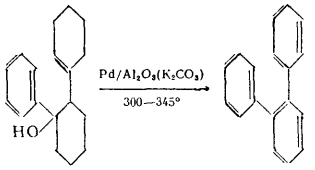


When 3-*p*-tolyl-3-menthene is heated with sulphur at 220°–230°, 3,4'-dimethyl-6-isopropylbiphenyl is formed with an 85% yield [220]. If the temperature is raised by 100°, however, considerable amounts of 2,6,9,9-tetramethylfluorene and 2,6,9-trimethylphenanthrene are formed. Similar condensations may occur in the case of a cyclic substituent. Dehydrogenation of 1-phenyl-2-cyclohexylcyclohexanol with selenium gives the triphenylene con-

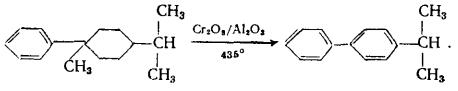
densed system[234]:



However, aromatisation of one of the isomeric 1-phenyl-2-(cyclohexen-1'-yl)cyclohexanols-1 (m.p. 58°–59°) using a Pd/Al_2O_3 catalyst pre-boiled with a 5% solution of K_2CO_3 gives *o*-terphenyl (yield 63%)[250]:

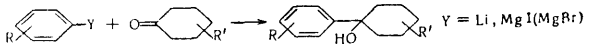


3. In some cases dehydrogenation may be accompanied by elimination or migration of alkyl and alkenyl substituents. 1,4-Diphenyl-5-vinylcyclohex-1-ene is converted to *p*-terphenyl (yield 86.5%) over 30% Pd/C at 320°[241]. An example of the migration of an alkyl group on dehydrogenation with sulphur has been mentioned above. In the case of an alkyl-aryl *gem*-substitution an alkyl group is usually eliminated[230,253,255,256] and this has served as a basis for a patented method of preparation of 4-alkylbiphenyls by dehydrogenation of 1-alkyl-1-phenyl-4-alkylcyclohexanes[256]:

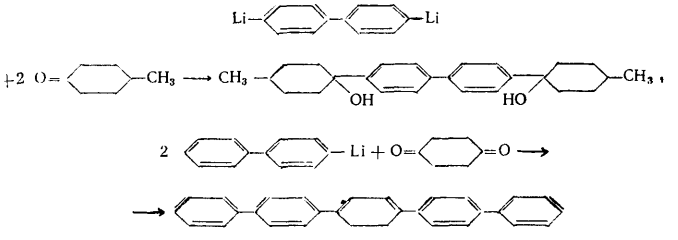


4. In isolated instances polyphenyl hydrocarbons can be prepared from derivatives of hydroaromatic hydrocarbons; when 4-bromo-4'-cyclohexylbiphenyl is dehydrogenated with selenium, the bromine atom is replaced by a hydrogen atom and *p*-terphenyl is formed[238].

Dehydrogenation is the final stage in the synthesis of polyphenyl hydrocarbons and the polycyclic chain molecule must be first constructed. Some methods of obtaining the initial hydroaromatic compound consist in linking separate cyclic molecules, others involve cyclisation and formation of new rings. Rings can be linked by the following methods: organometallic synthesis of the Grignard type, cycloalkylation of aromatic compounds, reduction of cyclic ketones to pinacols, and polymerisation of cycloolefines or cyclodienes. The first method is the most general, the number of rings being increased by interaction of cyclohexanes with aryllithium or arylmagnesium halide:

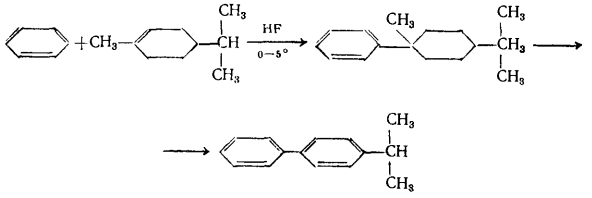


The use of dilithiobiphenyl[218], cyclohexane-1,4-dione[187], and bicyclohexyl-4,4'-dione makes it possible to lengthen the cyclic chain in two directions at once:

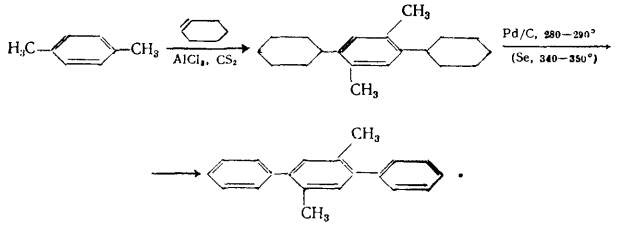


The wide scope of this method is demonstrated by the synthesis of a whole range of *m*-diarylbenzenes based on 3-ethoxycyclohex-2-en-1-one[242,244–247]

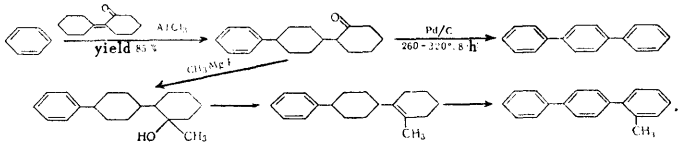
Cycloalkylation has been used repeatedly for the preparation of intermediate products in the synthesis of *p*-polyphenyl hydrocarbons[73,231,232,237,248,256,264,266]. Dihydroterpenes or dihydroterpene alcohols in the presence of HF have been recommended for the alkylation of benzene to yield 4-alkylbiphenyls[256]:



Alkylation of *p*-xylene with cyclohexene in the presence of $AlCl_3$ gives 2,5'-dimethyl-*p*-terphenyl[264]:

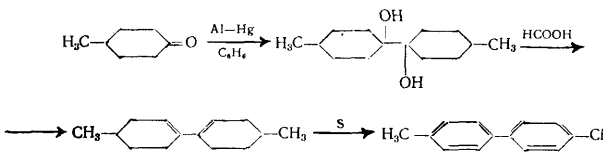


Condensation of benzene with cyclohexyl bromide has been used for the preparation of *p*-terphenyl[237]. The use of cyclohexylidenecyclohexanone for the synthesis of *p*-terphenyls is of interest[248]:



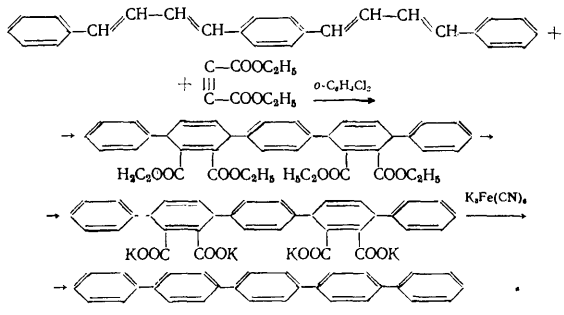
In some cases successful alkylation is achieved by the cyclohexyl ester of *p*-toluenesulphonic acid[266].

Much has been published on the cycloalkylation reaction, usually in connection with the use of dehydrogenation to prove the structure of the products obtained. Only in isolated cases are these products important as starting materials for polyphenyl synthesis. The same applies to polymerisation of unsaturated cyclic compounds[219,258]. The reduction of cyclohexanones to pinacols has been used successfully for the preparation of symmetrical biphenyls[228]:

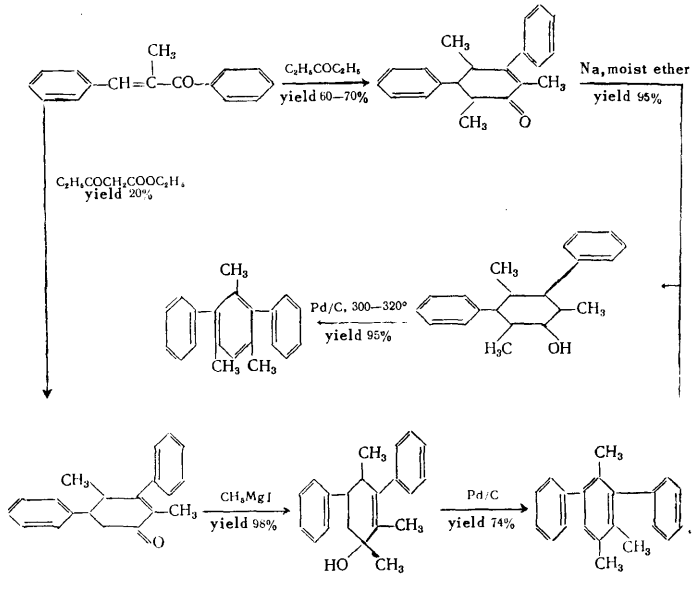


Any other type of construction of a polynuclear chain is based primarily on the diene synthesis and the Michael reaction in which new rings are formed by cocyclisation of the aliphatic parts of the initial molecules to form a contin-

uous chain with the already existing rings. The diene synthesis is very convenient for the preparation of polyphenyl hydrocarbons, but sometimes difficulties are encountered due to the relative unavailability of the starting materials; various polyphenyls have been synthesised by this method up to and including quinquiphenyls [241,249,260,261,263,267], *p*-quinquiphenyl, for example, being prepared as follows:

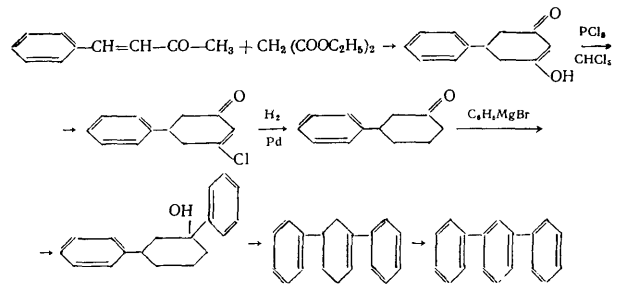


The Michael condensation has been used for the preparation of isomeric trimethyl-*m*-terphenyls [249]:

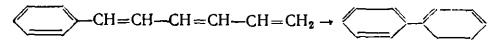


Condensation of *α*-benzylidene-*α'*-phenylacetone with malonic ester gives compounds of the *p*-terphenyl group [235].

Formation of hydroaromatic ketones as intermediates permits further lengthening of the chain by means of organometallic reagents; this forms the basis of a method for the preparation of *m*-terphenyl [80]:



Another method of forming a bicyclic molecule consists of cyclisation of 1-phenylhexa-1,3,5-triene over Al_2O_3 at 350° [259]:



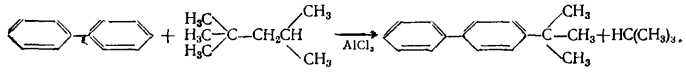
III. SYNTHESES WITHOUT ALTERATION OF THE AROMATIC CARBON SKELETON

1. Alkylation

The alkylation of biphenyl is the cheapest method for the preparation of many potentially useful industrial compounds [254,268-273]. Biphenyl reacts with olefines and alkyl halides in the presence of $AlCl_3$ usually giving a misture of mono-, di-, and sometimes even trialkylbiphenyls [268,269,274,275]. 2,4,4-Trimethylpent-2-ene taken in equimolar proportion at 70°–75° gives a 32.5% yield of alkyl derivatives with 52.6% mono-, 29.9% di-, and 17.5% tris-2,4,4-trimethylpent-2-yl-biphenyls [269]. Condensation with n-hexyl bromide in hexane yields mono- and di-hexylbiphenyls with an overall yield of 80% [275].

When biphenyl is alkylated with but-2-ene in the presence of $BF_3 . H_3PO_4$ catalyst in the molar ratio biphenyl : but-2-ene : catalyst = 1–4 : 1 : 0.2–0.3 at 50–100°, the main products are monobutylbiphenyls [276]. Their yield is 58–60% and they constitute 92% of the alkylate. Above 70° but-2-ene undergoes isomerisation and the product is therefore a mixture of *p*-s- and *p*-t-butylbiphenyl whose relative amounts depend on the reaction conditions.

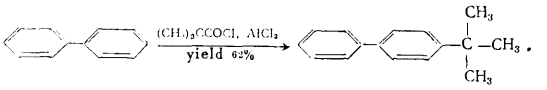
Biphenyl can also be alkylated by the saturated hydrocarbon 2,2,4-trimethylpentane in the presence of $AlCl_3$ to give mono-t-butylphenyls from which the *p*-isomer can be isolated by freezing out in 27% yield [277]:



When alcohols, in excess, act on biphenyl in the presence of H_3PO_4 catalyst with heating for 10–20 h [278], the main products are *p*-monoalkylbiphenyls (yield up to 60%). The optimum temperature is determined by the structure of the alcohol; it is 120°–125° for pentanols and 90°–110° for butanols. The rate of reaction increases from normal to tertiary alcohols. When iso-alcohols are used, isomerisation leads to the formation of t-alkylbiphenyls. When BF_3 catalyst is used, the reaction takes places in two stages [273,279]: (1) a molecular compound $2ROH . BF_3$ is formed when the cooled alcohol is saturated with boron fluoride, and (2) biphenyl is alkylated by the $2ROH . BF_3$ complex at 162°–170°. Under normal pressure, monosubstitution in the *p*-position predominates, but at 25–30 atm the amount of *p*,*p'*-dialkyl derivatives increases up to 46–50%. The total yield of alkylbiphenyls is 80–98%. Longer heating and a larger excess of alcohol are necessary when $BF_3 . H_3PO_4$ is used, but the yield does not exceed 65%. The authors postulate intermediate formation of unsaturated hydrocarbons, or of carbonium ions directly, e.g. by dissociation of the molecular compound of a normal alcohol with BF_3.

Interesting examples of alkylation are the preparation of ethylbiphenyls by heating biphenyl and diethylbenzene with $AlCl_3$ at 80°–110° [281] and the formation of *p*-t-butylbiphenyl in attempted acylation of biphenyl with trimethylacetyl

chloride[282]:



2. Preparation by way of Aliphatic-Aromatic Ketones

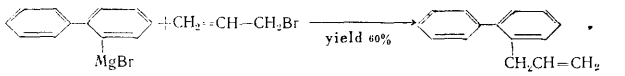
Alkyl substituted polyphenyls can be prepared by reduction of aliphatic-aromatic ketones, e.g. *p*-alkylbiphenyls containing up to 18 carbon atoms in the side chain[64,281,283-287], 4-alkyl-*m*-terphenyls[288], and 4-butyl-*o*-terphenyl[289]. The reduction is effected by the Clemmensen method with zinc amalgam and hydrochloric acid[281,284,286,287,289], hydrazine hydrate and alkali[288], hydroxylamine and metalic potassium[285], or with hydriodic acid[283]. Sometimes it is desirable or even necessary to obtain first the corresponding carbinol, dehydration of which also permits the synthesis of polyphenyl hydrocarbons with an unsaturated side chain[281,290]. For example, when 2',2'-diacetylbiphenyl is reduced by the Clemmensen method, the product is anomalous[290] and the diactyl compound is therefore first converted with lithium aluminiumhydride to the glycol, which is then dehydrated to 2,2'-divinylbiphenyl which, in turn, is hydrogenated to 2,2'-diethylbiphenyl.

When aliphatic-aromatic ketones react with Grignard reagents, tertiary alcohols and polyphenyls with branched side chains are formed. This method has been suggested for the preparation of *p*-isopropenyl-[219-293] and *p*,*p*'-diisopropenylbiphenyl[294] used as monomers for polymer syntheses. Similarly, (1-butyloctadecyl)biphenyl has been prepared from stearoylbiphenyl and butylmagnesium chloride[287]. The alcohols and glycols are dehydrated by the usual methods taking into account the tendency of the olefines formed to polymerise[271,281,287,291-298].

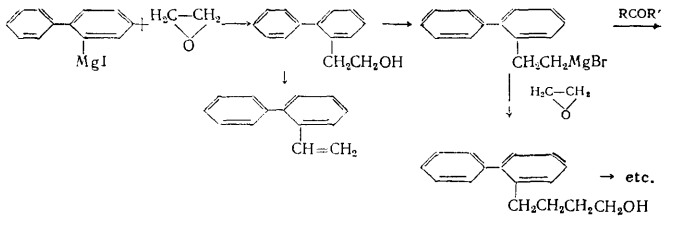
3. Grignard Synthesis from Polyphenyl Halides

The reactions of polyphenylmagnesium halides with aliphatic aldehydes and ketones give a variety of alkyl- and alkenyl-polyphenyls, in particular alkylbiphenyls[76,254,257,281,291-293,299-302]. This method has been used for the preparation of *o*-substituted biphenyls with large unsaturated substituents[300,301], which it would be difficult or impossible to prepare by any other method.

If the carbonyl compound is replaced by an allyl halide, it is possible to introduce a double bond into the β-position of the side chain[302]:



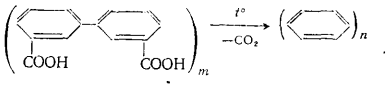
Ethylene oxide provides further possibilities[302]:



Moreover, organometallic compounds undergo direct alkylation: the reaction between CH_3HSO_4 and 4-lithio-*p*-terphenyl gives a 67% yield of 4-methyl-*p*-terphenyl[222], and biphenyl-2-yl magnesium iodide and diethyl sulphate give 42% of 2-ethylbiphenyl[254].

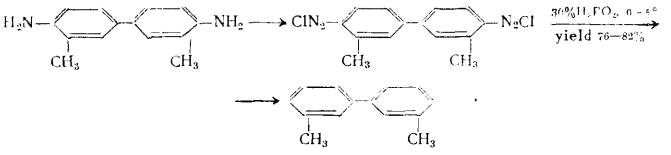
4. Preparation by Elimination of Functional Groups

Polyphenyl hydrocarbons can be prepared by decarboxylation of aromatic acids; *o*-terphenyl is formed on dry distillation of the silver salt of *o*-terphenyl-2-carboxylic acid[135]. The anhydride of *p*-quaterphenyl-2',3'-dicarboxylic acid gives a hydrocarbon when heated with basic copper carbonate in quinoline[267]. The polymer obtained by deamination of 4,4'-diaminobiphenyl-3,3'-dicarboxylic acid at an elevated temperature is, apparently, converted to polyphenyl[98-100]:

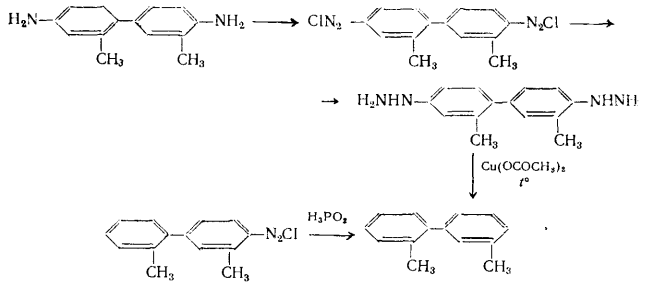


Fission of various carbonyl compounds has been used for the preparation of 3',6'-dimethyl-[303] and unsubstituted *o*-terphenyl[218].

The hydroxyl and methoxy groups can be removed by distillation with zinc dust[304-306]. Another way of converting phenols into hydrocarbons is by reduction of the corresponding phosphates[307]: diethyl-*p*-biphenyl phosphate is reduced by alkali metal in liquid ammonia to biphenyl with a yield of 75–80%. Deamination is also achieved by the usual methods[308]: diazotised *o*-tolidine is reduced by 30% hypophosphorous acid to 3,3'-dimethylbiphenyl[309]:



2,3'-Dimethylbenzidine is first converted to the corresponding hydrazine derivative which is oxidised by distillation with copper acetate to 2,3'-dimethylbiphenyl[137]. The latter can also be prepared from hypophosphorous acid and 4-amino-2',3-dimethylbiphenyl[310]:

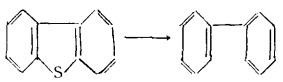


The diazonium salt of 4-amino-*p*-terphenyl forms *p*-terphenyl when reduced by sodium stannite in an alkaline medium[311]. Benzidine yields biphenyl when it is diazotised and treated either with Cu_2O in $H_2SO_4-CH_3COOH$[312], or with hypophosphorous acid, or boiling ethyl alcohol[308] (yield 23–80%).

There are also isolated examples of dehalogenation[81], elimination of selenium[313], elimination of silicon-containing groups[314], etc.

5. Preparation from Heterocyclic Compounds

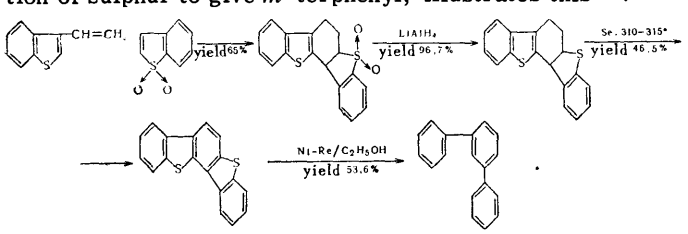
The molecules of some heterocyclic compounds with five-membered rings contain polyphenyl hydrocarbon skeletons. Dibenzothiophene can be regarded as biphenyl with a sulphur bridge in the 2,2'-position; on treatment with Raney nickel in boiling alcohol, an atom of sulphur is replaced by 2 atoms of hydrogen and biphenyl is formed in 97.5% yield[315]:



Dibenzoselenophene under these conditions gives a low yield of biphenyl but if the reaction is carried out in 10–20% solution of alcohol in benzene with nickel (approximately 20 times the weight of the sample), the yield rises to 87%[313]. Dibenzoselenophene oxide and dichloride give 72% biphenyl.

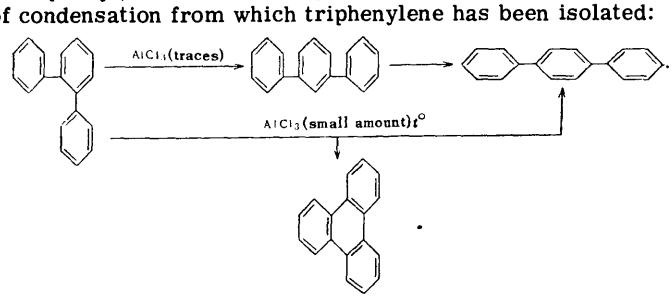
When dibenzothiophene is boiled with lithium (molar ratio 1 : 2.2) in dioxane, 30.5% is converted to biphenyl[316]. Dibenzofuran gives only *o*-hydroxybiphenyl when treated with lithium.

Elimination of sulphur by nickel may be accompanied by replacement of functional groups in the initial compound by hydrogen. Simultaneous dehalogenation causes 2-bromodibenzothiophene to yield approximately 35% of biphenyl[316]. An interesting series of conversions, which includes the preparation of a heterocyclic compound followed by elimination of sulphur to give *m*-terphenyl, illustrates this[317]:



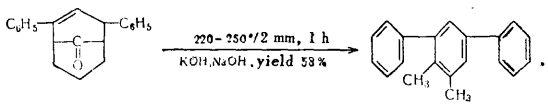
IV. SYNTHESES WITH ISOMERISATION AND FISSION OF THE CYCLIC CARBON SKELETON

These reactions are used only in exceptional cases. *o*-Terphenyl undergoes isomerisation under the influence of traces of $AlCl_3$[218], forming first *m*-terphenyl which then gradually changes to the *p*-isomer. Further reactions occur simultaneously and become more important the higher the temperature and the larger the amount of $AlCl_3$. The main product of heating with molten $AlCl_3$–NaCl at 130° is *p*-terphenyl, but at 200° the predominant products are those of condensation from which triphenylene has been isolated:

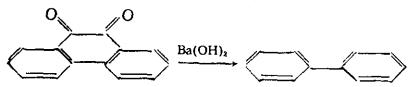


No triphenylene is formed on pyrolysis of *o*-terphenyl without $AlCl_3$.

Examples of ring fission of cyclic molecules are the preparation of 4,5'-dimethyl-*m*-terphenyl by heating 2,4-diphenylbicyclo[3,3,1]-non-2-en-9-one with a mixture of NaOH and KOH in vacuo[318],



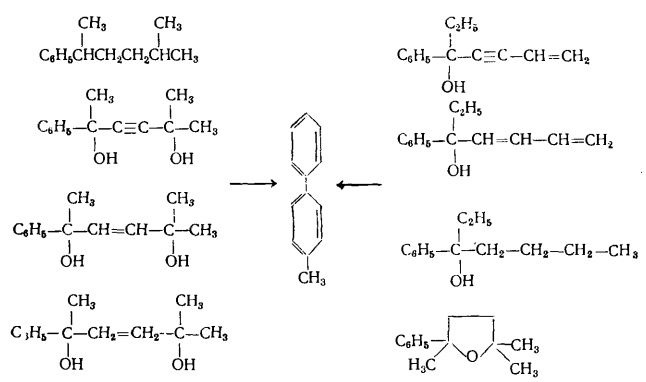
and the preparation of biphenyl by thermal fission of phenanthrenequinone with $Ba(OH)_2$[319].



Biphenyls can also be formed by catalytic dehydrogenation of bicyclic compounds containing a seven-membered ring[320,321].

V. SYNTHESES WITH FORMATION OF INDIVIDUAL UNITS OF THE POLYPHENYL CHAIN (DEHYDROCYCLISATION)

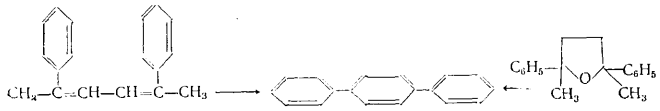
The side chain of aliphatic aromatic compounds which contains not less than 6 carbon atoms can be cyclised on a chromium-aluminium catalyst into a further aromatic ring which is not condensed with the already existing rings in the initial molecule[322–326]. This process can be applied to oxygen containing compounds (glycols, tetrahydrofurans, alcohols) as well as to hydrocarbons. The water which is split out during the reaction does not hinder the aromatisation.



The best yield of 4-methylbiphenyl from the various substances shown above using an $MgO/Cr_2O_3/Al_2O_3$ (2 : 18 : 80) catalyst is obtained with 2,2,5-trimethyl-5-phenyltetrahydrofuran (550°, 0.36 kg of catalyst per litre per hour)[322]. Under other conditions (HF or H_2SO_4) the latter is cyclised to a mixture of 1,2,4-trimethylnaphthalene and 1,1,4-trimethyl-1,2,3,4-tetrahydronaphthalene[327].

Terphenyls can be synthesised from diaryl-substituted compounds with sufficiently long aliphatic side chains[328,329]: 2,5-diphenyl-hexa-2,4-diene and 2,5-dimethyl-2,5-diphenyltetrahydrofuran undergo aromatisation at 530° with the

same catalyst to give *p*-terphenyl in 45–50% yield:



The limits of application of catalytic dehydrocyclisation to polyphenyl synthesis are at present difficult to establish as the reactions cited are among the first examples reported. When higher paraffins and olefines, or alkylbenzenes with shorter side chains, undergo this reaction, the products consist of condensed systems. The reaction has been studied in greater detail in these cases.

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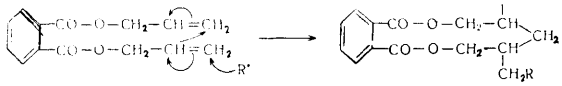
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POLYMERISATION OF UNCONJUGATED DIENES

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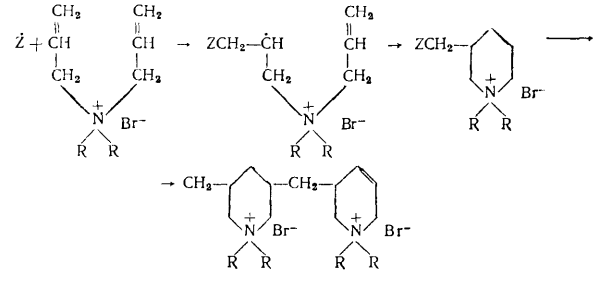
Ring closure during the polymerisation of compounds containing isolated double bonds was first proposed by Simpson[1] to explain the structure of the soluble poly(diallyl *o*-phthalate), obtained at low degree of polymerisation. A year later Howard[2] demonstrated the "intramolecular cross-linking" of some of this ester, during peroxide-induced polymerisation, giving an eleven-membered ring, and possibly some of the ten- and twelve-membered ring compounds:



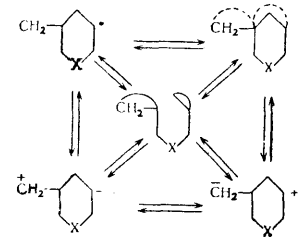
Later, Simpson and Holt[3,4] investigated the polymerisation, under the same conditions, of the diallyl and di-β-methylallyl esters of oxalic, malonic, succinic, glutaric, adipic, azelaic, sebacic, carbonic, and the three phthalic acids.

Polymers from such esters have recently been shown to be typical of many polymers from compounds containing two isolated double bonds, being abnormally soluble in organic solvents and showing little unsaturation. Many such polymers turn into equally soluble transparent plastics at high temperature and pressure.

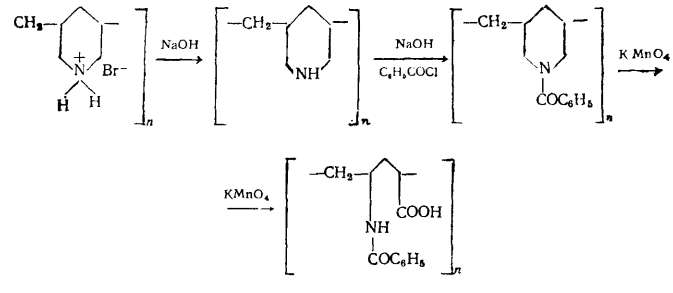
Butler and his coworkers[5-13] investigated the free-radical polymerisation of many allyl and methylallyl derivatives of quaternary ammonium salts, with the initial purpose of making strongly basic ion-exchange resins. Monoallyl derivatives did not polymerise at all, tri- and tetraallyl derivatives gave insoluble three-dimensional polymers, but the polymers from diallyl derivatives dissolved readily in water and ethanol[10-12]. This refuted the general assumption that polymers from monomers with one double bond are relatively soluble, while those from monomers with two or more double bonds are sparingly soluble or insoluble[15]. The effects of the initiator type and concentration, the nature of the anion, the amount of solvent, and the presence of oxygen, etc., on the polymerisation of compounds containing two double bonds, and the hydrogenation of polymers, were also studied[5-14]. Molecular-weight determination was complicated by the polyelectrolyte nature of the polymers. Butler and Angelo[11] found that polymerisation is most efficient if initiated by 2–3 wt.% of t-butyl peroxide or an azo compound, and continued for 48 h at about 60°. They concluded that free radicals initiate polymerisation of the diallyl derivatives to soluble products of relatively low molecular weight and a low degree of unsaturation, the mechanism they suggested involves radical chain propagation by a succession of intra- and intermolecular steps. Methylene and 3,5-disubstituted piperidinium groups alternate in the saturated, unbranched chain of the product, five- and six-membered rings being preferentially formed:

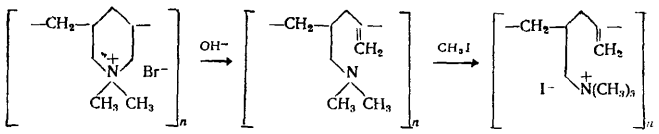


Butler[14] explained the strong tendency of 1,6-dienes to polymerise, in comparison with compounds containing only one double bond, in terms of mesomerism:

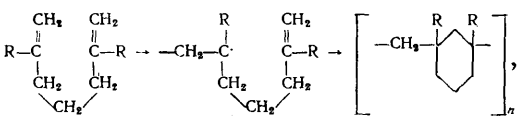


In order to establish the structures of the polymers, Butler et al.[13] investigated the degradation products of poly(diallylammonium bromide) and poly(diallyldimethylammonium bromide):

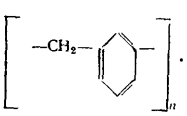




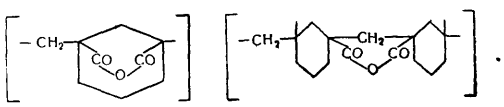
Recently Butler's terminology has gained wide acceptance, such terms as "cyclopolymerisation", "cyclopolymers", "cyclocopolymers", and "cyclocatalysts" appearing in the literature, and his mechanism has been applied to many other polymerisations, involving different initiators and catalysts, and producing chains containing rings of five or more atoms. Marvel and Vest[16] confirmed Butler's mechanism by obtaining polymers, soluble in organic solvents, from α,α'-dimethylenepimelic acid, its methyl and ethyl esters, and, recently, its nitrile and amide. Free-radical initiation was successful with solids, solutions, and emulsions. The authors' proposed mechanism is:



where R = COOH, $COOCH_3$, $COOC_2H_5$, CN, or $CONH_2$. The ring was aromatised by heating with potassium perchlorate in a sealed tube:



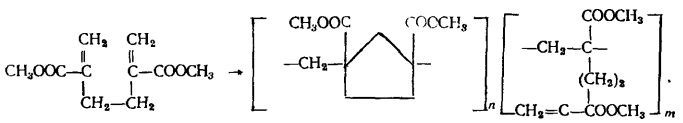
Polymerised dimethyl α,α'-dimethylenepimelate had an intrinsic viscosity, $[\eta]$, of 0.73 in chloroform, m.p. 300° (measured in a sealed tube, as for all polymers described), and a molecular weight of $2-3 \times 10^5$. For the polymerised diethyl ester, m.p. 125°–135°, $[\eta]$ was 0.14 in chloroform. The infra-red spectra of both polymers indicated negligible unsaturation. The products of dehydrogenation with potassium perchlorate showed infra-red peaks at 1620, 1595, and 1500 cm^{-1} and ultra-violet peaks at 255 and 240 mμ, characteristic of aromatic compounds and supporting the accepted mechanism of polymerisation[11]. Heating the poly(diethyl ester) at 300° caused no depolymerisation, a new soluble polymer forming, with infra-red bands characteristic of the acid-anhydride group. The authors suggested possible structures for the chain units:



The dinitrile of α,α'-dimethylenepimelic acid underwent free-radical polymerisation in dimethylformamide[17]. The polymer had an intrinsic viscosity of 0.655 in that solvent. Its unsaturation was virtually limited to the cyano groups, and it was more stable to heat than most polynitriles[18]; it darkened after several hours above 300°, but 80% of the polymer remained.

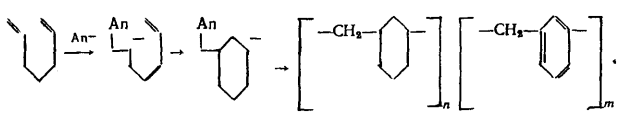
The polymer from the corresponding diamide[17] was exceptional in being insoluble in organic solvents. Any infra-red absorption bands due to the C=C bond were masked by those of the carbonyl group. The authors supposed the polymer to be cyclic, attributing its insolubility to extensive hydrogen bonding and not to a three-dimensional structure. The diamide, like the dinitrile, forms partially soluble copolymers with acrylonitrile or methyl acrylate; these are saturated, and stable up to about 250°.

Under similar conditions Marvel and Vest[17] obtained from dimethyl α,α'-dimethyleneadipate a polymer with little residual unsaturation, melting between 110° and 120°, of intrinsic viscosity 0.21 in benzene. 10% of the monomer units were in the form of open chains, and the rest as five-membered rings:

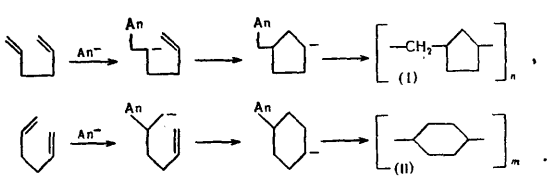


Marvel and Vest[17] noted that only soluble polymers are formed from emulsions or solutions of unconjugated dienes, but that polymerisation of the solid always gives some insoluble product.

In 1958 Marvel and Stille[19,20] polymerised hepta-1.6-diene with a mixed catalyst of aluminium isobutoxide and titanium tetrachloride. The product, of high molecular weight, melted at 210°–230°, dissolved readily in benzene, and formed films from this solvent. For $Al(iso\text{-}C_4H_9)_3$: $TiCl_4$ ratios of 1 : 1 and 1 : 3, $[\eta]$ = 0.2 and 0.4 respectively. Infra-red spectra showed that only 4–10% of the monomer units retained one of the two double bonds. Infra-red and ultra-violet spectra showed the product of degradation with potassium perchlorate (e.g. at 390° for 16 h in a sealed tube) to contain *meta*-substituted aromatic rings:



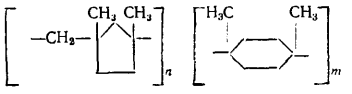
Hexa-1,5-diene gave a rubber-like polymer melting at 85°–90°, soluble only to the extent of 40 wt.% in benzene; for the soluble fraction, $[\eta]$ = 0.23. Comparison of the infra-red spectra of the monomer and the soluble polymer fraction showed that 5–8% of the monomer units retained one double bond. Of the structures proposed by the authors, (II) is believed the less likely, on account of the unstable anionic intermediate:



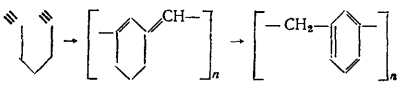
2,5-Diphenylhexa-1,5-diene gave similar soluble polymers of low molecular weight when polymerised by cationic or free-radical initiators[21].

Although 2,5-dimethylhexa-1,5-diene is one of the α,α'-disubstituted dienes, not polymerised by complex metal alkyl catalysts, Marvel and Stille[19] obtained from it a polymer of relatively low molecular weight (10000), soluble in some organic solvents, melting at 80°–85°, and of intrinsic viscosity 0.1. Of the monomer units, 3–13%

retained their unsaturation. Two structures were proposed:

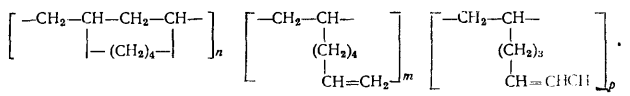


On thermal, free radical, cationic, or anionic initiation, 2,6-diphenylhepta-1,6-diene gave soluble polymers melting between 140° and 300°, for which $[\eta] = 0.19-0.49$.[21] From hepta-1,6-diyne and a Ziegler catalyst, Stille[21] obtained polymers of molecular weight 10 000–20 000, which were converted to polybenzyl on heating with palladised charcoal:

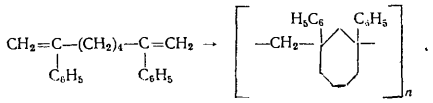


A British patent[22] describes polymerisation by complex metal alkyl catalysts of penta-1,4-diene, hexa-1,5-diene, octa-1,7-diene, and deca-1,9-diene, but does not indicate structures. A Belgian patent[23] describes copolymerisation of penta-1,4-diene, hexa-1,5-diene, and octa-1,4,7-triene with several olefines, using the same catalysts.

Marvel and Garrison[24] studied the polymerisation by complex metal alkyl catalysts of dienes of type $CH_2=CH-(CH_2)_n-CH=CH_2$, where n = 4, 12, 14, and 18. Soluble and insoluble fractions were obtained. The former was of low molecular weight and had an intrinsic viscosity of ~0.1; the latter was distinctly unsaturated and swelled considerably in benzene, indicating few cross-linkages. Extension of the polymerisation time gave only three-dimensional structures. Quantitative infra-red spectrometry and bromination showed that the soluble polymer fraction contained cyclic, vinyl, and vinylidene units:



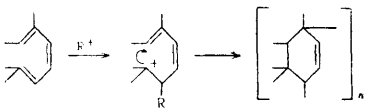
Polymerisation of, e.g. 2,7-diphenylocta-1,7-diene by a Ziegler or cationic catalyst apparently gave, at a low extent of polymerisation, cyclic polymers[21]:



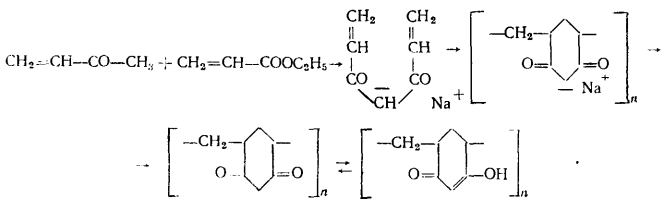
Marvel concluded that unconjugated dienes with three atoms separating the double bonds usually give soluble linear polymers with a six-membered ring unit. Fewer separating atoms may lead to a five-membered ring unit, but this is formed with difficulty and is accompanied by unsaturated open chain units. More than three separating atoms cause seven-membered rings to be formed, but with even more difficulty. Rings of more than seven members are very uncommon.

The conversion of *allo*ocimene (2,6-dimethylocta-2,4,6-triene) by various catalysts to soluble polymers of still unknown structure is well established[25-27]. Marvel and his coworkers[28] recently catalysed this polymerisation, with aluminium isobutoxide and titanium tetrachloride, in heptane at 15°. The amorphous, fibrous product, of intrinsic viscosity 1.0–1.2, melted between 120° and 154°, dissolved in organic solvents, and formed fairly strong films at 150° and 35 kg cm^{-2}. Traces of phenyl-β-naphthylamine reduced its tendency to atmospheric oxidation. Above 200° the polymer reverted to *allo*ocimene in 70% yield; infra-red spectra showed it to contain double bonds with a *trans*-configuration.

Jones[29] polymerised *allo*ocimene, by means of boron trifluoride etherate, to a soluble polymer, softening at 68°–70° and melting at 85°–87° and 70 kg cm^{-2} pressure; extrusion of the melt gave brittle fibres. The author suggested that one double bond takes part in the polymerisation and proposed a cationic mechanism:

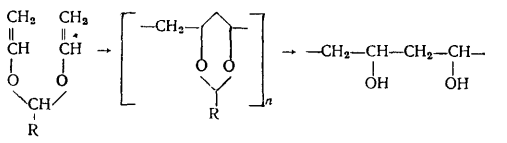


Jones[30] did not obtain diacroylmethane or its sodium salt from the Claisen condensation of methyl vinyl ketone with ethyl acrylate, since a polymer of the salt was formed at once, and was converted by acetic acid to polydiacroylmethane, made up of alternating methylene and dihydro-4,6-dihydroxy-*m*-phenylene units:



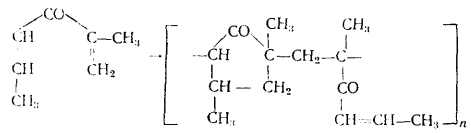
This polymer is soluble and of low molecular weight (2000), melts at 190°, and readily forms films; its infra-red spectrum indicates little unsaturation. Potentiometric titration showed that 48% of the polymer was present as enol, and polymeric azo dyes could be prepared from it. As the polymerisation proceeds at ordinary temperatures in the presence of air and free-radical inhibitors, the author inferred an anionic mechanism.

Divinylacetals have recently been converted to cyclic polymers[31-33] by peroxide initiators. Polydivinylformal is a white powder melting between 85° and 120°, and polydivinylbutyral is colourless and rubber-like. All the polydivinylacetals obtained dissolve readily in most organic solvents and show their saturation by not reacting with hydrogen or bromine. Hydrolysis gives polyvinyl alcohol:



Copolymers of divinylacetals with styrene, vinyl acetate, or acrylonitrile are soluble and fusible, with strong adhesive properties; the copolymer of divinylbutyral and styrene melts between 105° and 116°. Cyclic copolymerisation of two divinyl monomers is possible, as was shown for divinylformal and divinylacetal[32]. Matsoyan and Avetyan[34] also investigated the radical polymerisation of 2-methylhexa-1,4-diene-3-one, alternate molecules appa-

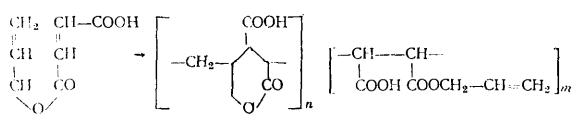
rently undergoing vinyl polymerisation of the isopropenyl group or ring closure:



The authors attribute this mechanism to steric hindrance of the formation of a complete chain of five-membered rings. The polymer is a white powder melting at 145°–150°, readily soluble in organic solvents, and of intrinsic viscosity 0.11 in benzene. Ozonolysis and bromination indicated about 25% unsaturation, relative to the monomer. 2,5-Dimethylhexa-1,4-diene-3-one polymerises in the same way.

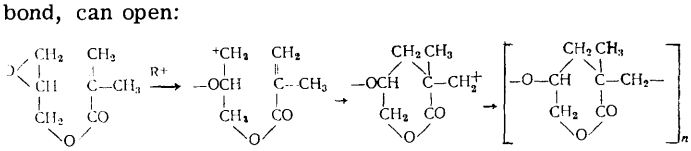
Arbuzova and her coworkers[35] obtained linear polymers (in reactions without solvent) from radical initiators and pure divinylformal, divinylacetal, and divinylbutyral; cyclic structures were indicated by analytical data and physical properties. With similar initiators, divinylbenzal gave a polymer of low molecular weight, in which methylene groups alternate with 3-phenyl-2,4-dioxacyclohex-1,5-diyl groups[36].

Arbuzova and Rostovskii[37,38] studied the cyclic polymerisation of a series of symmetrical and unsymmetrical 1,5- and 1,6-dienes, such as divinylacetals, monoallyl esters of unsaturated acids, and vinyl crotonate. Polymerisation (without solvent) of pure monoallyl maleate and citraconate in the presence of peroxide initiators gave 40–50% yields of linear polymers, soluble in dioxan, dimethylformamide, and other organic solvents; that from the maleate had a molecular weight of 15 000, determined from the rate of sedimentation, and an intrinsic viscosity of 0.156. About 25% of the units contained allylic double bonds:



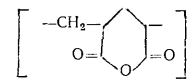
Azo-compound-initiators cause solutions of vinyl *trans*-crotonate and cinnamate to give linear polymers; one specimen of polyvinyl crotonate, of intrinsic viscosity 0.31, contained five- and six-membered lactone and ester units.

Arbuzova and Efremova[39] established a new type of cyclic polymerisation by means of the action of ionic catalysts on glycidyl esters of acrylic and methacrylic acids. The ethylene oxide (oxiran) ring, as well as the double bond, can open:



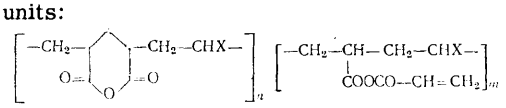
Glycidyl methacrylate was converted by boron trifluoride etherate and hydroquinone to a soluble polymer of low molecular weight. The radical-initiated polymerisation of glycidyl esters of unsaturated acids involves only the double bond[40].

Crawshaw and Butler[41] obtained polymers from acrylic anhydride on radical initiation in solution; these dissolved in organic solvents, and had molecular weights from several thousand to 95 000. The infra-red spectrum of the hygroscopic white powder produced indicated inappreciable unsaturation, and the authors consider the structural unit to be derived from α-methylglutaric anhydride:



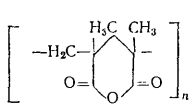
The polymer was hydrolysed to a polyacrylic acid of more regular structure than that of specimens made by radical-initiated polymerisation of acrylic acid.

From acrylic anhydride and radical initiators in organic solvents, Jones[42] obtained a linear polymer of molecular weight 200 000 which was hygroscopic and readily soluble in polar organic solvents such as dimethylformamide, γ-butyrolactone, *N*-methylpyrrolidone, and dimethyl sulphate. Acrylic anhydride is often considered as a cross-linking agent, copolymerising with other vinyl monomers[42,43]. In its homopolymerisation all the vinyl groups are equivalent, and cyclise and polymerise readily (cyclopolymerisation). On addition of a monomer of different reactivity, cyclic polymerisation is reduced and is accompanied by formation of up to 50% of three-dimensional non-cyclic units:



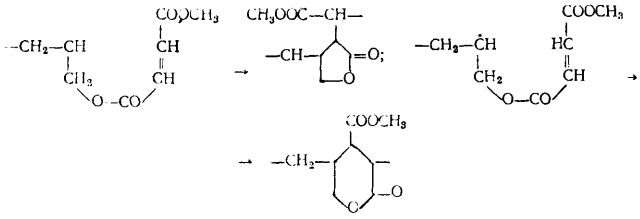
By controlling acrylic anhydride polymerisation with compounds such as trimethylamine or dimethyl sulphide, Jones[42] obtained a linear polymer of high molecular weight, and also a polymer of molecular weight 20 000, soluble in ethanol and dioxan, with considerable unsaturation evidently due to end groups, and readily converted to transparent granules and films at 180° and 1750 kg cm^{-2} pressure. The polymer enters into many reactions characteristic of anhydrides, its reactivity decreasing as its molecular weight increases, possibly on account of intermolecular steric hindrance. Hydrolysis with water for some days at room temperature made films of linear polyacrylic anhydride identical with those of polyacrylic acid.

Using Butler's method[41], Bresler and Koton and their coworkers[45] obtained from methacrylic anhydride an 80% yield of a cyclic polymer of high molecular weight, soluble in dimethylformamide, melting at 200°, and of intrinsic viscosity 0.6–0.8. Polymethacrylic acid gave the same product when heated:

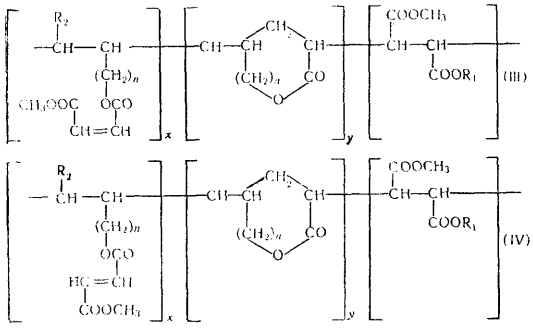


Soluble polymers from unsymmetrical 1,6-dienes are well known. Allyl acrylate is polymerised in dilute solution by benzoyl peroxide[46], allyl methacrylate by benzoyl peroxide on ultra-violet irradiation at 350–380 mμ [47,48], and α-, β-, and γ-methylallyl methacrylates by benzoyl peroxide in toluene[49]. The authors did not propose cyclic structures for the polymers. Butler et al.[50] polymerised pure methyl allyl, methyl but-2-enyl, and methyl but-3-enyl maleates and fumarates by means of benzoyl peroxide (without solvent), obtaining readily soluble linear polymers of low molecular weight and considerable unsaturation (37–77%). The authors suggested structural units derived from γ-butyrolactone, δ-valerolactone, and

ϵ-caprolactone:

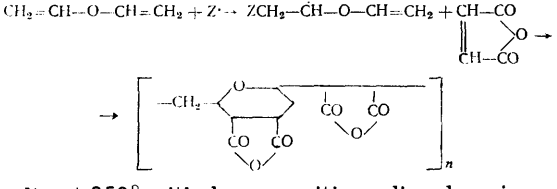


Possible units derived from the maleates (III) and the fumarates (IV) are:

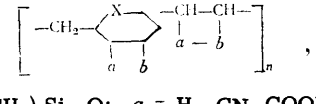


The authors[50] consider that unsymmetrical dienes form cyclic polymers to a lesser degree than do symmetrical dienes. The extent of cyclisation for the six unsymmetrical monomers studied varied from 23% to 60%, compared with complex-cyclisation of symmetrical monomers capable of forming six-membered rings.

Butler[14] studied the copolymerisation of 1,4-dienes with olefines, the mechanism of which is very similar to that described above. Divinyl ether and maleic anhydride copolymerise by a radical mechanism to a linear polyanhydride:

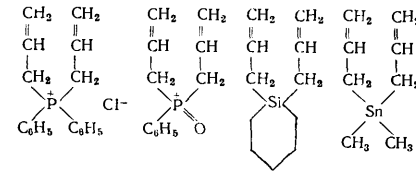


This melts at 350° with decomposition, dissolves in acetone and dimethylformamide, has intrinsic viscosity 0.175 in dimethylformamide, is only slightly unsaturated, and undergoes the usual reactions of anhydrides. Other 1,4-dienes used were divinyldimethylsilane, divinyl sulphone, and divinylcyclopentamethylenesilane; other olefines were fumaronitrile, fumaryl chloride, dimethyl fumarate, diethyl maleate, and vinyl acetate. The copolymers were linear and saturated, the author proposing the structure:

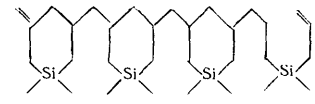


where X = CH_2, $(CH_3)_2Si$, O; *a* = H, CN, COOR; *b* = CN, COOR; *a* - *b* = CO–O–CO.

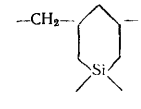
Butler and his coworkers[21] obtained soluble cyclic polymers of low unsaturation, in the presence of radicals or Ziegler catalysts, from the following unconjugated dienes:



Kolesnikov and his coworkers[51] attempted to polymerise diallyldialkylsilanes, the structural analogues of 4,4-dialkylhepta-1,6-dienes. Triethylaluminium and titanium tetrachloride in a non-polar solvent converted diallyldiethylsilane to a soluble polymer of low molecular weight and little residual unsaturation, for which was proposed the tetrameric structure:



Topchiev and his coworkers[52] obtained polymers of unknown structure, mainly liquids, from diallyldimethylsilane and diallylmethylphenylsilane in the presence of a Ziegler catalyst. Bogomol'nii[53] polymerised diallyldiphenylsilane and diallyldimethylsilane with a Ziegler catalyst at 70°–80°, obtaining from the latter a rubber-like polymer soluble to the extent of 80% in benzene, and of intrinsic viscosity 0.05–0.09 in that solvent. Some 20–25% of the units contained a double bond; the author considered the predominant unit to be



Mikulasova and Hrivik[54] showed that diallyldimethylsilane yields a cyclic polymer in the presence of t-butyl peroxide. Marvel and his coworkers[21] have stated that a cyclic polymer of relatively high molecular weight is produced by a Ziegler catalyst from diallyldimethylsilane.

Research into cyclopolymerisation is continuously increasing. Some of these new and unusual polymers, with alternating cyclic and linear segments, will certainly be of practical value.

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OCCURRENCE OF THE TRANSURANIUM ELEMENTS IN NATURE

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INTRODUCTION

Whether uranium, with an atomic number of 92, is last in the series of elements or whether elements heavier than uranium can exist, is a question that has interested chemists ever since the discovery of the Periodic Law. The correct answer to this question could only be given by contemporary chemists and physicists when heavy elements lying beyond uranium in the Periodic Table were produced artificially in 1940. Mendeleev himself admitted the possibility of extending the Periodic System to include elements heavier than uranium. Later, a great deal of work was devoted to the investigation of the possible existence of transuranium elements and to the structure of their electron shells.

Attempts to detect transuranium elements in nature have been made for some time. Reports have repeatedly appeared in the literature concerning their natural occurrence but, after more careful study, these data have mostly proved to be incorrect. The chief reasons for the lack of success were: (1) unreliable methods of investigation; (2) wrong placing of the transuranium elements in the Periodic Table, whereby they would constitute a group of analogues to osmium, iridium, and platinum, i.e. element 93 should be the analogue of manganese and rhenium, element 94, of ruthenium and osmium, and so on. On this hypothesis, Loring and Druce[1-4] undertook a search for element 93 in samples of manganese and rhenium using X-ray analysis. They discovered weak lines in the wave-length region predicted for this element. They considered this as proof (though not conclusive) of the presence of element 93 in manganese ores. It was established later that the observed lines belonged to other elements.

In 1934 Koblic reported[5] that he had discovered element 93, for which he proposed the name "bohemium", in

Bohemian (Jachymov) pitchblende. Koblic assumed that the element he had discovered was an isotope of element 93 with a mass number of 240. He was of the opinion that pitchblende contained 1% of bohemium. However, X-ray and chemical analysis[6] showed that the material obtained by him was really a mixture of silver tungstate and vanadate, after which Koblic withdrew any claim to the discovery[7].

In 1938, Hulubei and Gauchois[8,9] reported the discovery of element 93 in various minerals such as betafite, monazite, columbite, and tantalite. They suggested the name "sequanium" for this element, but their findings also were not subsequently confirmed.

In 1941 Wahl[10], while making a mass-spectrometric study of columbite and tantalite, noticed a line corresponding to mass 237, which he supposed to belong to an isotope of the first transuranium element. However, this assertion also proved to be mistaken.

It has now been established that all the neptunium isotopes are β-emitters of short half-life; this is the obstacle to their discovery. Only neptunium-237 emits α-particles, with a half-life of 2.20×10^6 years, but even this period of time is small compared with the age of the earth. Even if this element once existed in rocks, then owing to its insufficiently long half-life it would have disintegrated long ago. The neptunium-237 found in natural uranium specimens is formed continuously from the uranium.

After 1936 several reports also appeared in the literature, concerning the occurrence of element 94 in minerals. During studies of the radioactivity of various minerals, pleochroic halos of abnormal radii ($\sim 5\ \mu$)[11-18] and α-particles with a path-length of 1.8 and 2.9 cm in air[19-21] were discovered; the path-lengths agreed with those calculated for the particles producing the pleochroic halos. This activity could not be ascribed to any radioactive element known at that time. Chemical investigation revealed two characteristic features of the source of the radiation: (1) precipitation with sulphides in strongly acid solutions; (2) volatility from hot oxidising solutions (HNO_3, H_2SO_4).

These two activities corresponding to path-lengths of 1.8 and 2.9 cm are always found in constant ratio, throughout all chemical operations. The chemical similarity apparently indicated the existence of two isotopes of the same element, or the presence of nuclear isomerism. The constant quantitative relationship between the activities is evidence of a genetic link between the two isotopes, one giving rise to the other by one α-disintegration and two β-disintegrations, as is the case with $^{238}U-^{234}U$ and $^{232}Th-^{228}Th$:

$$^{238}U \xrightarrow{\alpha} {}^{234}Th \xrightarrow{\beta^-} {}^{234}Pa \xrightarrow{\beta^-} {}^{234}U, \quad (1)$$

$$^{232}Th \xrightarrow{\alpha} {}^{228}Ra \xrightarrow{\beta^-} {}^{228}Ac \xrightarrow{\beta^-} {}^{228}Th. \quad (2)$$

On account of the chemical similarity of the unknown source to osmium and because of the fact that osmium itself is inactive, Schintlmeister assumed that the activity was due to eka-osmium, i.e. element 94. From the laws of α-disintegration of heavy nuclei, Schintlmeister[22] inferred that the α-particles with path-lengths of 1.8 and 2.9 cm could be ascribed to nuclei of element 94 with masses 244 and 240. This question was given much attention in Germany, since it was considered possible that the parent element could be split under the influence of neutrons, and the natural raw materials could thus be used to produce energy.

After study of the properties of plutonium had shown that they differed from those of osmium, it became evident that Schintlmeister's assumptions were mistaken. Furthermore, with the heavy elements, the energy of α-disintegration of β-stable nuclei has a tendency to increase rather than to decrease as Schintlmeister supposed.

According to Levinos and Kurtis[23], certain technical uranium preparations have a greater specific activity than the corresponding pure compounds. They ascribed the difference to the presence of an α-active impurity, with chemical properties similar to those of uranium, which could be element 94. However, this suggestion was not confirmed and was apparently mistaken.

Reports by Gysae and Korschling[24,25] that they had found α-emitters, with α-particle path-lengths of ~ 2 and 3 cm, whose properties were similar to those of plutonium or neptunium, were similarly not authenticated. It is rather doubtful whether any isotope of plutonium or neptunium would emit α-particles of such low energy.

The first sound evidence for the existence of transuranium elements in nature was provided by the work of Seaborg and Perlman, dating from 1942, i.e. from a time when the properties of the transuranium elements had already been thoroughly studied.

OCCURRENCE OF PLUTONIUM IN NATURE

The occurrence of plutonium in nature was first proved by Seaborg and Perlman[26] in 1942. The isolation of plutonium from 400 g of pitchblende which contains ~ 40 different elements was based on the property of Pu^{III} and Pu^{IV} to coprecipitate with the rare-earth fluorides. In the highest oxidation state, Pu^{VI}, plutonium behaves like uranium; it does not coprecipitate with the fluorides of the lanthanides, but, in contrast to uranium, it is reduced considerably more easily. By means of repeated oxidation-reduction cycles the plutonium was separated from the uranium and from the other elements. Using radiochemical methods, it was shown that the concentration of plutonium in natural specimens is 10^{-14} g per g of uranium.

Since the half-lives of plutonium isotopes are very small in comparison with the age of the earth, the amount of plutonium found cannot be the undecayed residue of the originally existing element. Its presence can be explained by radioactive processes which continuously produce a minute quantity of plutonium, while the observed quantity represents the equilibrium between formation and disintegration of the element. The most probable mode of formation of this element may be expressed as follows:

$$^{238}U(n, \gamma)^{239}U \xrightarrow[23\ min]{\beta^-} {}^{239}Np \xrightarrow[2{\cdot}3\ days]{\beta^-} {}^{239}Pu. \quad (3)$$

In particular, the reaction involving neutron capture by the ^{238}U nuclei is identical with that which occurs in a uranium reactor during the production of plutonium. It follows from reaction (3) that the isotope ^{239}Pu constitutes the main part of the plutonium formed in minerals. Garner, Boner, and Seaborg[27] obtained much the same result in isolating plutonium from carnotite (see Table).

Using a Wilson cloud-chamber, Chatterjee[28] also observed minute quantities of ^{239}Pu in uraninite.

These first data on the existence of plutonium in nature were of a preliminary character and could not claim high accuracy. The isolation of such small concentrations of plutonium presented great difficulty, because its separation from macro-impurities and especially from radioelements whose activity is more than 10^6 times greater

Summary of results on the extraction of plutonium from ores.

Ore	Sample, g	Uranium content, %	Quantity extracted, counts min	Chemical yield, %	Ratio × 10^{11} ^{239}Pu : ore	Ratio × 10^{11} ^{239}Pu : U	References
Uranium ore (Canada)	400	—	1.5	80	0.1*		26
Carnotite	5000		2.8	60	0.1		42
Uranium ore (Canada)	100	13.5	0.66	10	9.1	0.71	29
Congo	10	38	3.2	10	48	1.2	
Colorado	40	50	3.40	26	38	0.77	
Brazilian Monazite	1000	0.24	0.36	25	0.21	0.83	
N. Carolina	1000	1.64	0.3	17	0.59	0.36	
Colorado fergusonite	280	0.25	0.01	5	0.1	0.4	
Colorado carnotite	500	10	0.15	12	0.4	0.04	
Congo uranium ore	2000	45.3	43.0	4.3	70±7	1.5±0.2	30
Uranium ore	2000	43.5	400	33.3	87	2.0±0.3	31

* Yield is much too low. After recalculation by Peppard, the ratio ^{239}Pu: ore becomes 5.5×10^{-13}.

than that of plutonium, was a very complex operation. Seaborg and Levine[29] later worked with samples of uranium pitchblende, monazite, carnotite, and fergusonite. Isolation of the plutonium was achieved by means of lanthanum fluoride cycles. The results obtained by Seaborg and Levine are also included in the Table.

It is interesting to note that the ratio of plutonium to uranium was found to be almost constant ($\sim 10^{-11}$) in pitchblende and monazite, where the uranium content varies from 50 to 0.24%, and much lower in carnotite and fergusonite. This is evidence both that the plutonium content is dependent on the uranium content and also of the probability of the formation of natural plutonium from ^{238}U according to Eqn. (3), as discussed above.

Peppard et al.[30] have also studied the extraction of plutonium from uranium ores. They found 7.0 ± 0.7 parts of plutonium per 10^{12} parts of ore concentrate. After certain corrections, made by Peppard, their values agree fairly well with the data from the original work of Seaborg and Perlman[26], in which it was assumed that the extraction was very efficient. If new data on the behaviour of plutonium are taken into account, recalculation of their results gives one part of plutonium per 1.8×10^{12} parts of ore or a ratio of ^{239}Pu to ore of 5.5×10^{-13}.

Starik et al.[31] worked out a new scheme to increase the yield of plutonium during its purification, since the fluoride method is very complex and gives low yields. In Peppard's work[30], the activity of the isolated natural plutonium was only of the order of tens of counts per minute. The method of isolation devised by Starik involves coprecipitation of plutonium with uranium diacetate and subsequent extraction with diethyl ether. By this method it was possible to remove all the residual α-active elements. From 2 kg of ore, Starik's method gave a quantity of plutonium which had an activity of 400 counts per minute; this corresponds to a ^{239}Pu : U ratio of $(2.0 \pm 0.3) \times 10^{-11}$. This result is shown in the Table, together with the earlier data.

The work of Peppard et al.[30], in which microgramme quantities of plutonium were isolated, enabled a detailed study of the isotopic composition of natural plutonium to be made. Since, according to the work of Seaborg and Perlman[26], about 100 tons of ore are needed to produce 1 mg of plutonium, the extraction was carried out from the aqueous waste produced during the working up of uranium pitchblende to uranium. The aqueous waste contains practically all the soluble parts of the ore concentrate, except for the uranium, the concentration of which has been reduced to negligible proportions.

Extraction of plutonium from this raw material, which is a saturated solution of metal nitrates together in nitric acid, was accomplished by extraction with tributyl phosphate, followed by purification using TTA-cycles*. Plutonium-239 was identified by measurement of the energy of the α-particles, determination of the ability of the material to undergo fission under the influence of thermal neutrons, mass-spectrographic analysis, and radiochemical methods. None of these methods detected any isotopes other than ^{239}Pu. The upper limit for the ratio of ^{238}Pu to ore (Congo and Canadian ore) had been established earlier by Levine and Seaborg as $1 : 4 \times 10^{15}$ (by weight). Measurement of the α-particle energy with a multi-channel differential pulse analyser enabled Peppard to establish the upper limit for the ratio ^{238}Pu : ^{239}Pu as less than 3×10^{-6} (by weight). Since ^{238}Pu can only arise as a result of a two-fold β-disintegration of ^{238}U,

$$^{238}U \xrightarrow{\beta^-} {}^{238}Np \xrightarrow{\beta^-} {}^{238}Pu, \qquad (4)$$

the calculated half-life of ^{238}U for the emission of two β-particles is 10^{18} years, which is in full agreement with other data[32]. The presence of plutonium isotopes with larger atomic masses was investigated by determining the ability of a sample of natural plutonium to undergo fission when irradiated with neutrons in a uranium pile, and by mass-spectrography. However, these experiments did not give a positive result, so that one is justified in assuming that the content of heavy plutonium isotopes is below the limit of sensitivity of the methods of determination. The upper limit for the sum of the isotopes ^{240}Pu, ^{241}Pu, and ^{244}Pu cannot exceed 1% (mass-spectrographic data) and that for ^{242}Pu (on the basis if neutron irradiation), cannot exceed 0.01%.

The general behaviour of α-active nuclei give grounds for assuming the presence of the isotope ^{244}Pu in nature, since, with increase in mass number, the half-life of β-stable α-active nuclei increases. The isotope ^{244}Pu is β-stable and emits α-particles with an energy of 4.5–4.7 MeV with a half-life of $(7 \pm 2) \times 10^7$ years[33]. This is comparatively small, so that the probability of detecting ^{244}Pu in nature is negligible. If ^{244}Pu does exist in nature, it must be accompanied by equilibrium quantities of ^{240}U, ^{240}Np, ^{240}Pu, ^{236}U, ^{232}Th, and all its decay products. The upper limit for ^{244}Pu in Congo uranium pitchblende is not more than one part in 1.4×10^{13} parts of ore. Since the chemical properties of plutonium in its lower oxidation states are similar to those of thorium and the rare-earth elements, it is possible that the long-lived isotope ^{244}Pu might be found in the ores of these elements. It is for the same reason that ^{244}Pu was not found in uranium ores. In a sample of plutonium extracted from Brazilian monazite the proportion of ^{244}Pu is not more than 14% of the ^{239}Pu content. Peppard, taking the half-life of ^{244}Pu to be 10^8 years, calculated the possible content of this isotope in Brazilian monazite and found the upper limit to be $1 : 3.6 \times \times 10^{11}$ (by weight), which indicates the incidental presence of large quantities of this isotope at the time of formation of the earth. Diamond and Barnes[34] found the half-life of ^{244}Pu to be $(7.6 \pm 2) \times 10^7$ years. If the formation of the

* TTA-cycles consist, essentially, of the formation of chelate complexes of Pu^{IV} with thenolytrifluoroacetone, which can be isolated by extraction with benzene.

elements took place 5.5×10^9 years ago and the quantity of ^{244}Pu formed at that time was half that of ^{232}Th, the ratio of ^{232}Th to ^{244}Pu in thorium ores today would be 10^{32}. If the half-life is taken as the upper limit, 9.6×10^7 years, a quantity of ore corresponding to 34 kg of thorium could contain 10^{-13} g of ^{244}Pu.

NEUTRON SOURCES

The question of neutron sources is very important in a study of the origin of natural plutonium. The chief source of neutrons in uranium ores is undoubtedly the spontaneous fission of uranium. If it is assumed that ^{239}Pu arose as a result of neutron capture by ^{238}U nuclei, the observed ^{239}Pu content is too great to be due to the neutron flux produced by spontaneous fission of natural uranium (24.2 ± 0.5 fissions per gramme per hour)[35]. Taking the equilibrium ratio of $^{239}Pu : ^{238}U$ to be $(1.5 \pm 0.2) \times 10^{-11}$, Peppard calculated the quantity of ^{239}Pu (128 ± 17 atoms) formed per hour from 1 g of ^{238}U. The number of neutrons produced by uranium fission is insufficient for the formation of this quantity. However, the neutron flux produced by the interaction of high energy α-particles from elements of the uranium series with light elements such as, for example, boron, oxygen, magnesium, silicon, etc., present in the ore can supplement this deficiency. In addition, to the total number of neutrons must be added those produced by the action of cosmic rays and those from the ^{235}U nuclei. The ^{235}U nucleus can capture a neutron and itself undergo fission with formation of several neutrons (an average of 2.5).

The average intensity of these sources can only be established with great difficulty, owing to the many variables (depth of the ore deposit, uranium content, content of boron, oxygen, magnesium, silicon, etc.). If one reckons that an average of two neutrons are produced per fission[36] and that the fission constant of uranium is 1.1×10^{16}, we can conclude that 1 g of ^{238}U emits approximately 1.1 neutrons per minute by spontaneous fission. Thus 100 g of ore containing 13.5% of uranium produce about 15 neutrons per minute; 1 g of uranium, together with its decay products, emit approximately 6×10^6 α-particles per minute, the maximum energy of which is in the range 4.2–7.68 MeV. 100 g of Canadian pitchblende, containing 13.5% of uranium, can produce 15–20 neutrons per minute as a result of (α, n)-reactions. The yield is appreciably greater if light elements are present in high concentration. The neutron intensity from cosmic radiation is 0.1 neutron per cm^2 per min at sea level[37]. Although this quantity can be greater, the proportion of neutrons from cosmic radiation in the total neutron flux is relatively small.

It should be emphasised that these estimates of neutron flux are very approximate, if only because the fission constant of uranium, according to different authors[38,39], may differ from that quoted above. In addition, the estimate of the neutron flux from (α, n)-reactions is subject to errors due to insufficient knowledge of the chemical composition of the ores and to lack of accurate information about the yield of (α, n)-reactions. Consequently, the actual intensity of the main sources may differ appreciably from that described.

In ores with high uranium content, more neutrons are emitted by uranium fission and by (α, n)-reactions, but the ratio of ^{239}Pu to ^{238}U generally remains constant. In monazite ores the situation is different. In view of their low uranium concentration, the ratio of plutonium to uranium can be less than in uraninite. If the main source of neutrons is taken to be the spontaneous fission of ^{238}U, the other elements present in the ore capture a large quantity of neutrons and only a small proportion is captured by the ^{238}U. Neutrons from the spontaneous fission of ^{232}Th do not make up this deficiency, because the spontaneous fission of ^{232}Th is many times less frequent than that of uranium ($T_{1/2}$ = = 10^{20} years)[40] so that the contribution of neutrons from (α, n)-reactions is of great importance. 1 g of thorium in equilibrium with its decay products emits 1.5×10^6 α-particles per minute able to take part in (α, n)-reactions. For a constant ratio of ^{239}Pu to uranium, 1 g of North Carolina monazite must absorb about 0.4 neutron per minute. Since the ratio of U to Th in thorium ores is less, the role of neutrons from (α, n)-reactions is greater. These neutrons form the greater part of the neutron flux. Thus the number of neutrons produced in 1 g of uranium in monazite ores is greater than in uranium ores and the neutrons absorbed by other nuclei are fairly well compensated for.

It follows from this that a high content of elements absorbing neutrons and a low uranium (or thorium) content reduce the ratio of ^{239}Pu to uranium. This rule is well confirmed in the case of carnotite and fergusonite. The chemical composition of carnotite is $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$ and that of fergusonite is $Y(Nb, Ta)O_4$ with some erbium, cerium, dysprosium, iron, calcium, and uranium. These elements absorb neutrons with a high effective cross-section which may explain the low ratio of ^{239}Pu to uranium in carnotite and fergusonite, since only a small part of the total number of neutrons are used to produce ^{239}Pu.

OCCURRENCE OF NEPTUNIUM IN NATURE

It follows from the nuclear properties of neptunium that none of its isotopes can exist in nature, unless it was formed comparatively recently or is formed continuously by radioactive processes in thorium and uranium ores. The fact that ^{239}Pu is present in nature means that traces of 2.3 day ^{239}Np should be found in uranium minerals because of its continuous formation from ^{238}U by neutron capture. In addition, Seaborg has shown that ^{237}Np can be present in uranium minerals; this is the parent isotope of the $(4n+1)$ radioactive series, resulting from the formation of β-active ^{237}U by the action of fast neutrons on uranium in the nuclear reaction

$$^{238}U(n, 2n)^{237}U \xrightarrow{\beta^-} {}^{237}Np. \qquad (5)$$

Since only a very small proportion of neutrons have the necessary energy of about 6 MeV, the possibility of ^{237}Np formation is low. As a result, the concentration of ^{237}Np is many times less than that of natural plutonium-239. Peppard et al.[41] succeeded in extracting ^{237}Np from the residues of the processing of Congo pitchblende.

It is well known that when ^{237}Np disintegrates, ^{229}Th is formed ($T_{1/2} = 7.34 \times 10^3$ years), while ^{238}U disintegrates to ^{230}Th ($T_{1/2} = 8.0 \times 10^4$ years):

$$^{237}Np \xrightarrow{\alpha} {}^{233}Pa \xrightarrow{\beta^-} {}^{233}U \xrightarrow{\alpha} {}^{229}Th, \qquad (6)$$

$$^{238}U \xrightarrow{\alpha} {}^{234}Th \xrightarrow{\beta^-} {}^{234}Pa \xrightarrow{\beta^-} {}^{234}U \xrightarrow{\alpha} {}^{230}Th. \qquad (7)$$

The half-lives of these isotopes are fairly large compared with the age of the mineral seam but are nevertheless small in relation to the age of the earth. It follows from this that the ratio of the activities of ^{229}Th to ^{230}Th and ^{237}Np to ^{238}U should be similar, if the ^{229}Th isotope were formed from ^{237}Np only by reaction (6). However, ^{229}Th can also be formed in another way.

Garner et al.[27] suggested that in uranium ores having a small thorium content another member of the $(4n+1)$ radioactive series can be produced — the isotope ^{223}U, formed by the reaction

$$^{232}Th(n, \gamma)^{233}Th \xrightarrow[23\cdot5\ min]{\beta^-} {}^{233}Pa \xrightarrow[27\cdot4\ days]{\beta^-} {}^{233}U. \qquad (8)$$

This disintegrates further, giving ^{229}Th. The extent to which this reaction affects the ^{229}Th content is not known at present.

The weight ratios of thorium to uranium in Congo ore, established by Peppard et al.[41], are given below:

$$^{229}Th : {}^{230}Th = (3.4 \pm 0.3) \times 10^{-10};$$

$$^{229}Th : {}^{232}Th = (4.0 \pm 0.6) \times 10^{-11};$$

$$^{233}U : {}^{238}U = (1.3 \pm 0.2) \times 10^{-13}.$$

Assuming that all the ^{233}U found in the ore was formed by reaction (6), it was established that in Congo pitchblende ^{237}Np is present in concentrations corresponding to a ratio of ^{237}Np to ^{238}U of $(1.8 \pm 0.4) \times 10^{-12}$. However, the possibility that reaction (8) has an appreciable influence is not excluded. In such a case, the actual concentration of ^{237}Np could differ from that quoted.

OCCURRENCE OF THE TRANSPLUTONIUM ELEMENTS IN NATURE

Other elements can be produced in the earth's crust in a similar manner to ^{239}Pu, ^{233}U, and ^{237}Np. The isotope ^{239}Pu can absorb further neutrons and be gradually converted to other transuranium elements:

$$^{239}Pu(n, \gamma)^{240}Pu(n, \gamma)^{241}Pu \xrightarrow{\beta^-} {}^{241}Am(n, \gamma)^{242}Am \xrightarrow{\beta^-} {}^{242}Cm.$$

Since the ^{239}Pu content of uranium and thorium minerals is very low and the neutron flux in these ores is too weak, i.e. it cannot be compared to that obtaining in a uranium reactor where these reactions take place easily, only theoretical data can at present be adduced concerning the presence of elements of atomic number greater than 94 as a result of (n, γ)-reactions.

It is possible that part of the ^{239}Pu is a decay product of a long-lived parent transplutonium element. Accurate data regarding this possibility are not available at present, but the energy of α-disintegration tends to increase as one passes to the heavier transuranium elements and the half-life is correspondingly reduced. Consequently, it does not seem possible that an isotope of plutonium or some other heavy element could exist in nature in a more or less stable state and hence there is little chance that ^{239}Pu could be formed as a decay product of a heavier, long-lived parent substance. Of the plutonium isotopes, ^{244}Pu is a possible exception. However, even its half-life is less by several powers of ten than the age of the earth. Of the other transplutonium elements, ^{247}Cm attracts attention. The isotope ^{247}Cm is β-stable and emits α-particles with a half-life greater than $(4-9) \times 10^7$ years[42]. From the laws governing spontaneous fission, it follows that the half-life for fission is greater than that of ^{255}Fm (6×10^8 years)[43]. The decay of ^{247}Cm proceeds as follows:

$$^{247}Cm \xrightarrow{\alpha} {}^{243}Pu \xrightarrow{\beta^-} {}^{243}Am \xrightarrow{\alpha} {}^{239}Np \xrightarrow{\beta^-} {}^{239}Pu \xrightarrow{\alpha} {}^{235}U.$$

If one assumes that the formation of the material of the earth took place $(5-9) \times 10^9$ years ago, the quantity of ^{247}Cm formed in that time, together with the heavier isotopes of the $(4n+3)$ radioactive series which disintegrate to give ^{247}Cm, can be estimated from the measured variations in the proportions of daughter isotopes with even mass numbers, namely $^{235}U : {}^{238}U$, reflected in the inconstancy of the $^{235}U : {}^{238}U$ ratio.

Since curium resembles the rare earths in its chemical properties, ^{247}Cm should be sought in the rare-earth minerals. If it is assumed that ^{247}Cm does not disintegrate completely in a period of time greater than forty times the half-life, then in order that ^{247}Cm should be found, it must have a half-life of at least 1.3×10^8 years. This assumes the age of the earth to be 5×10^9 years; if it is 9×10^9 years, the half-life of ^{247}Cm must be 2.2×10^8 years. Assuming that the time elapsing between the formation of ^{247}Cm and the distribution of curium and uranium among the separate mineral phases was less than 7 half-lives, a measurable change in the ratio $^{235}U : {}^{238}U$ (not less than 2%) can be observed in rare-earth minerals, in which the ratio rare earths : $U \geq 1000$. In older minerals or minerals with a low uranium content, this enrichment by ^{235}U will be more pronounced.

It is interesting to note that isotopes such as ^{244}Pu and ^{247}Cm, together with their decay products, could have been important sources of radioactive heat in the first 500 million years after their formation[44,45]. It has been calculated that when one atom of ^{244}Pu disintegrates to ^{232}Th, 6.28×10^{-13} cal are liberated, and when ^{247}Cm disintegrates to ^{235}U, 6.23×10^{-13} cal are liberated (65% of the energy in a β-disintegration is lost in the form of neutrinos).

Except for the long-lived isotopes ^{244}Pu and ^{247}Cm, the isotopes of the transuranium elements found in nature are formed from uranium and thorium either by radioactive decay or by neutron irradiation. Naturally, the question arises whether at some time elements heavier than uranium existed in nature and have not survived to the present day only because of their short half-life. This question, which is closely related to the problem of the formation of the elements, has not yet been settled. The discovery of technetium in the spectra of certain stars and the sun supported the theory that the heavy elements are being formed continuously in the stars by nuclear processes, since the longest-lived isotope of this element, ^{99}Tc, has a half-life of only 2.4×10^5 years. It is supposed that the formation of heavy elements occurs in the explosion of supernovae. A great step forward in this field was made by the study of class I supernovae[46,47]. These stars are characterised by a high maximum in their luminosity: 50–100 days after the maximum, the relation between the logarithm of the luminosity and time become linear during the next 600 days; in other words, the "half-life" is 55 ± 1 days[48]. This naturally suggests the idea that the energy of these stars comes from the disintegration of some isotope having a half-life of about 55 days. Such isotopes could be ^{7}Be or ^{89}Sr, but since their energy of decay is small (57 and 600 keV respectively), the quantity of the isotopes required to provide the enormous amount of energy radiated by the star would be such that the amount of disintegration products would considerably exceed their proportion present in the Universe[49,50]. In 1952, during the explosion of a hydrogen bomb[51], the isotope ^{254}Cf was observed; this is formed from uranium under the influence of a powerful neutron flux. ^{254}Cf is a β-stable isotope whose half-life of spontaneous fission is 56.2 ± 0.7 days[52], 60 ± 10 days[33], or 85 ± 15 days[43], in good agreement with the observed astrophysical value of 55 ± 1 days. α-Activity has not been observed, but this is natural, since theoretical considerations show the half-life of this isotope to be about 10^2 years for α-emission[43]. In one fission, 200 MeV are liberated

so that 10^{47} ergs (the energy radiated by a star) correspond to the disintegration of 10^{29} g of ^{254}Cf; this is in agreement with the observed distribution of the fission products in the Universe.

It is important to elucidate how ^{254}Cf is produced. One can assume that the process takes place in the same way as in the artificial production of the isotope, i.e. by the absorption of neutrons produced by nuclear reactions at stellar temperatures. The isotope ^{56}Fe, which is present in sufficient quantity in stellar material and which has a high capture cross-section for neutrons, captures neutrons up to the saturation point, which lies below the threshold of neutron instability; this occurs at $N = 0.7A$, $Z = 0.3A$. The nucleus produced undergoes β-disintegration and again absorbs a neutron. Because of the supersaturation with neutrons, the times [half-times? (Ed. of Translation)] of the β-disintegrations do not exceed 0.1 sec, so that the formation of ^{254}Cf takes about 7 sec. The explosion of a star has a velocity of about 10^3 km sec^{-1}. Since the radius of the star is $10^{10}-10^{11}$ cm, there is an interval of 10–100 sec, which is quite sufficient for the synthesis of ^{254}Cf to occur. Other classes of stars do not possess the necessary conditions for ^{254}Cf to be formed in sufficient quantity to have a decisive influence on their behaviour.

Other heavy elements are also produced in the explosion of supernovae. But because of their nuclear properties they cannot play a similar part in the behaviour of the star after the explosion. A possible exception is the ^{250}Cm isotope which resembles ^{254}Cf in many respects[52]. One can expect that it also decays predominantly by spontaneous fission and not by α-disintegration.

The predicted half-life for the α-disintegration of ^{250}Cm is about 10^{15} years and that for spontaneous fission $(1-10)\times 10^4$ years. The fission of ^{250}Cm could be an important source of energy in old "remains" of type I supernovae, such as the Crab nebula which is apparently the remains of the supernova of 1054. The Crab nebula radiates 5.7×10^{42} ergs year^{-1} or about 10^5 times less than at the initial instant. If the quantities of ^{254}Cf and ^{250}Cm formed in the explosion were equal, then the radiation produced at the present moment from the spontaneous fission of ^{250}Cm would be 10^{-5} of the initial energy of the ^{254}Cf and could be the source of all the energy radiated by the Crab nebula.

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